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A comparison study between the tenax trap and the canister collection methods for determination of volatile organic compounds

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ABSTRACT

Title of Thesis : **A comparison study between the Tenax trap and the Canister collection methods for determination of volatile organic compounds**

Name of Candidate: Li-Ching Lillian Hung
Master of Science in Environmental Science, 1989

Thesis and Abstract Approved: 9/8/89
Dr. B. Kebbekus Date
Associate Chairperson
Department of Chemical Engineering , Chmistry & Environmental Science
Co-Director of the Air Pollution Research Lab

A comparison between the analytical methods for determination of volatile organic compounds, using Tenax GC as an adsorbent and using stainless steel canister collection is made.

Sample collection, analytical system and procedures, data analyses, as well as their fortes and their drawbacks, etc., are discussed.

In addition, a brief description of the developmental history of the above methods as used in the Air Pollution Research Laboratory at the New Jersey Institute of Technology in Newark, New Jersey, is given.

A COMPARISON STUDY BETWEEN
THE TENAX TRAP AND THE CANISTER COLLECTION METHODS
FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

by

Li-Ching Lillian Hung

Thesis submitted to the Faculty of
the Graduate School of the New Jersey Institute of Technology in
partial fulfillment of the requirements for the degree of
Master of Science in Environmental Science
1989

APPROVAL SHEET

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1. INTRODUCTION

A. The importance of monitoring and analysis for volatile organic compounds (VOCs)

Volatile organic compounds comprise 31 out of the 129 priority pollutants that are designated by the U.S. Environmental Protection Agency (EPA) as shown in Table 1.01. They are considered harmful to continually exposed human beings [1]. In addition, the role of non-methane hydrocarbons in the formation of photochemical smog has been known since the early 1950s. Although the quantitative relationship between the atmospheric concentrations of hydrocarbons and oxides of nitrogen and those of the photochemical oxidants that they produce is still imperfectly understood, it is widely agreed that the most effective way to reduce the occurrence of smog is some form of VOC control. This strategy appears to apply nowadays all over the world [2]. Control measures are frequently based on techniques of monitoring and measurements of VOC concentrations in the ambient air.

Early methods for the analysis of individual atmospheric hydrocarbons usually involved freezing out the VOCs from a volume of air (typically 0.1-1.0 L) onto a precolumn packed with a chromatographic support at liquid oxygen or nitrogen temperature, the analysis often being limited to C_2-C_6 hydrocarbons [2]. For wider ranges of hydrocarbons (C_2-C_{16}) more sophisticated instrumentation for sampling as well as analysis is necessitated.

Two techniques of sampling are generally used:

a. Preconcentration of air samples by trapping on a suitable adsorbent, such as charcoal [3], graphitized carbon black [4], and Tenax [5], etc. Among these, the most commonly used material is Tenax because of its low affinity for water vapor and its good thermal stability.

b. Direct collection of whole air samples in containers, such as plastic bags made of Tedlar [6], glass bulbs [2], or stainless steel tanks, followed by in-laboratory concentration. However, Tedlar bags tend to contaminate the air samples with acetaldehyde and acetone [7], while the surface of plain stainless steel tanks is found to adsorb organic materials. Yet recently, the use of s.s. tanks has become predominant, since the technique of sampling in SUMMA passivated stainless steel canisters was introduced and was tested for satisfactory sample integrity and storage stability [8,9].

Samples of both types are then quantitated by high resolution gas chromatography equipped with specific detectors, such as Flame Ionization Detector (FID), Electron Capture Detector (ECD), or Photo-Ionization Detector (PID), etc.

B. The background of this comparison study

The analysis of atmospheric ambient air for VOCs has been of interest for the past few decades. There have been a wide variety of sampling and analytical methods for both preconcentrated air samples and whole air samples. However, these common methods still tend to yield erratic data, and none of them is evaluated as trouble-free.

This study is done with the intent to illuminate all the advantages as well as the disadvantages of the **Tenax trap method** and the **SUMMA polished Canister collection method**, which are the most common ones currently used by research laboratories conducting VOC analyses.

The study is based on the analytical data obtained during **THE NORTHEASTERN NEW JERSEY-STATEN ISLAND, NEW YORK URBAN AIR TOXICS ASSESSMENT PROJECT (SI/NJUATAP).**

The SI/NJ UATA project is co-sponsored by the U.S. EPA and the New Jersey Department of Environmental Protection (NJDEP), with sampling beginning in July, 1987.

Samples are collected every sixth day at sites. The NJIT Air Pollution Research Laboratory has taken responsibility for the sites at Carteret and Elizabeth, NJ.

The overall objective of the project is to characterize the air quality in the target regions for selected air pollutants. Ultimately, the data will be used for human exposure assessments [10].

C. The compounds of interest for VOC analysis are stipulated by the U. S. EPA [10], and are shown in Table 1.02 with their general properties.

Table 1.01---List of VOCs as priority pollutants designated by the EPA [1].

1	Acrolein
2	Acrylonitrile
3	Benzene
4	Bis (Chloromethyl) Ether
5	Bromoform
6	Carbon Tetrachloride
7	Chlorobenzene
8	Chlorodibromomethane
9	Chloroethane
10	2-Chloroethyl vinyl Ether
11	Chloroform
12	Dichlorobromomethane
13	Dichlorodifluoromethane
14	1,1-Dichloroethane
15	1,2-Dichloroethane
16	1,1-Dichloroethylene
17	1,2-Dichloropropane
18	1,3-Dichloropropylene
19	Ethylbenzene
20	Methyl Bromide
21	Methyl Chloride
22	Methylene Chloride
23	1,1,2,2-Tetrachloroethane
24	Tetrachloroethylene
25	Toluene
26	1,2-Trans-Dichloroethylene
27	1,1,1-Trichloroethane
28	1,1,2-Trichloroethane
29	Trichloroethylene
30	Trichlorofluoromethane
31	Vinyl Chloride

Table 1.02 Compounds of interest and their characteristics

Abbre-viation	Name/ Synonym	Formula	Mol.Wt	m.p.(^{o}C)	b.p.(^{o}C)
1. MECL	Methylchloride /Chloromethane	CH_3Cl	50.49	-97.73	-24.2
2. DCM	Methylenechloride /Dichloromethane	CH_2Cl_2	84.93	-95.1	40.0
3. C6	Hexane	$CH_3(CH_2)_4CH_3$	86.18	-95.0	68.95
4. CFOR	Chloroform /Trichloromethane	$CHCl_3$	119.38	-63.5	61.7
5. 111*	1,1,1-Trichloroethane /Methylchloroform	$CH_3:CCl_3$	133.41	-30.41	74.1
6. BZ	Benzene	C_6H_6	78.12	5.5	80.1
7. CCL4	Carbon tetrachloride /methane tetrachloride	CCl_4	153.82	-22.99	76.54
8. TRIC	Trichloroethylene	$ClCH:CCl_2$	131.39	-73	87
9. TOL	Toluene /methyl benzene	$CH_3C(CH)_5$	92.15	-95	110.6
10. PERC	Tetrachloroethylene /Perchloroethylene	$Cl_2C:CCl_2$	165.83	-19	121
11. PMX	p-Xylene & m-Xylene /1,4 & 1,3 dimethyl benzene	C_8H_{10}	106.17 106.17	13.26 -47.87	138.35 139.1
12. OX	o-Xylene /1,2-dimethyl benzene	C_8H_{10}	106.17	-25.18	144.4

2. DESCRIPTION OF THE TWO METHODS

A. Tenax trap method

a. Preparation of Tenax traps

i. Tenax-GC is a porous polymer, the characteristics of which are described in Table 2.01 [11]. Conditioning of the Tenax is important and is typically done by the suppliers before purchase as follows:

First, the Tenax is extracted with acetone, cyclohexane, and methanol sequentially for at least 8 hours in each solvent at a temperature of 300 ^{o}C. This treatment removes viscous liquid material from the Tenax.

Then it is dried at 120^{o}C under vacuum. It is ready to pack when it becomes free-flowing [12].

ii. Packing of Tenax traps

Tenax traps are prepared by filling stainless steel tubes of 1/4 inch (6.4 cm)OD by 7 inch long with 350 mg of the conditioned Tenax, which is retained in the traps with plugs of silanized glass wool.

The packed section of a trap is approximately 2.75 inches long only, about one third of the total length, and is deliberately placed away from the marked end that is to be inserted into a desorber furnace while being analyzed.

iii. Treatment of Tenax traps before use

The traps are attached to a manifold that is connected to a supply of prepurified grade (99.99 %) nitrogen. Nitrogen flow is adjusted to approximately 10 ml/min for each trap.

Any one trap, through which the nitrogen flow rate is above 12 ml/min or below 8 ml/min, should be removed and repacked. The manifold is then placed in an oven at 300^{o}C for 8 or more hours. Substantially more time (i.e., 3 days, usually) may be needed for traps filled with new Tenax [12].

iv. Blank test of Tenax traps

Randomly select one trap for a blank test.

If this trap is tested satisfactorily clean, all the traps on the manifold are considered ready for sampling. Then the traps are sealed at each end by use of compression connectors and plugs [12].

b. Tenax trap sampling

Samples are collected from ambient air at two sites, Carteret and Elizabeth, New Jersey.

Two parallel Tenax traps are used to collect 7 and 14 liters of air in 24 hours, at two different flow rates, 5 ml/min and 10 ml/min.

Two different flow rates are needed for the determination of breakthrough on Tenax.

Traps should be so attached in the sampling system that the marked ends will be the air inlet ends. Sampling must be started between 9 and 11 in the morning of the first sampling day, to keep the samples at the various sites on a common schedule, according to the protocol of the SI/NJ UATA Project [10]. Samples should be stored at room temperature and analyzed within two weeks (three at the most), after being brought back to the laboratory on the next day [12].

c. Sample analysis of the Tenax traps

i Equipment being used:

Thermal desorber : Tekmar 5000 automatic desorber

Gas chromatograph : Varian 3700 GC

Column: Hewlett Packard PONA Crosslinked Methyl fused silica capillary column, 0.21 mm x 50 m, with 0.5 micron of film thickness of OV-101

Detectors: Electron-capture detector (ECD) coupled with Flame ionization detector (FID)

Recorder: 2-pen recorder by Soltec co.

Utility needed:

Desorb gas: Helium of ultra-high purity, at a pressure 20 psi min. and a flow rate 10 ml/min.

Coolant: Liquid nitrogen, 25 psi.

Carrier gas: Helium of zero-grade at 2 ml/min.

Make-up gas: Nitrogen of zero-grade at 28ml/min.

Split ratio of gas flow between ECD and FID:1/10

ii. Analysis procedures

(1) Hooking up---Remove the plugs from the connectors at each end of the trap. Insert the trap into desorber furnace with the marked end down inside the furnace.

(2) Prepurge---The trap is purged with desorb gas (He) at 10 ml/min and ambient temperature for three min. for the purposes not only of dispersing any trapped water vapor, which would otherwisely spoil the GC column resolution, but also of removing the oxygen, thus preventing the Tenax from oxidation and artifact formation, consequently increasing its lifetime [13].

(3) Desorbing---The trap is heated at a desorption temperature of 210 ^{o}C and a flow rate of 10 ml/min.for 12 min. This displaces the desorbed VOCs from the steel trap to a cryogenic trap(Cryo-1), which has been cooled to -150 ^{o}C.

(4) Transfer---The Cryo-1 is heated to 210 ^{o}C,thus desorbing the cryogenically trapped VOCs to a second cryogenic trap (Cryo-2) at -150 ^{o}C for focusing, through a transfer line at 210 ^{o}C. The duration is 12 min. at a flow rate 1 ml/min.

(5) Injection---The Cryo-2 is then rapidly heated to 210 ^{o}C (in 0.5 min.) so injecting the VOCs onto the GC column.

Temperature of the column is then changed according to the following :

Initially 35 °C for 12 min., then increased at a gradient of 6 °C/min. up to 195 °C, then held for 5 min.

(6) Bake---The desorbed trap is baked for 15 min. at 225°C. This serves as a cleaning process and can be an alternate for the treatment stated in 2.A.a.iii for traps to be reused. For new traps, baking in an oven at 300 °C for 3 days is required to ensure cleanliness.

Steps (1) through (6) are considered as a cycle, and are automatically progressed, except step (1), by the Tekmar desorber processor.
The analytical system is shown schematically in Figure 2.01 [13].

d. Result generation : The detector signals are integrated and subsquently the VOC concentrations are calculated using an A/D converter board and software supplied by Interactive Microware Co. of State College, PA.

B. Canister collection method

As known at the incipient stage, sampling in canisters of plain stainless steel showed problems of chemical reactions of metal with certain reactive constituents in the atmospheric air samples [14].

In the past few years, the US EPA has conducted or sponsored a series of tests in regard to sample integrity and storage stability of the air samples collected in SUMMA polished canisters, and obtained successful results [8,9]. The air samples were spiked with numerous compounds, many of which are chlorinated VOCs, under simulated field conditions. The organic compounds that have been tested are listed in Table 2.02 [8,9].

The stainless steel canisters used for the SI/NJUATA project are those mentioned above, the interior surfaces of which have been treated by the Molectric SUMMA passivating process, in which a pure chrome-nickel oxide is formed on the surface [15].

Canisters of this kind are referred briefly as **"the Canisters"** hereinafter.

The Canisters in use are of 6 liter volume, maximum service pressure of 40 psig, by Scientic Instrumentation Specialists, Inc. When purchased, a stainless steel bellows valve, which is also internally SUMMA passivated,is usually furnished by the manufacturer and attached on the outlet of each Canister.

a. Cleaning---Contamination may occur in the sampling system, if the Canisters are not properly cleaned before use. The device is shown as in Figure 2.02. The cleaning procedure involves the following steps:

i Heating the Canisters to around 35 °C.

ii Evacuating the Canisters to less than 1 mm Hg. The duration of the evacuation, previously set at one hour as recommended by the EPA [16], now has been shortened to a few minutes, since experiments showed no better efficiency from longer evacuation time.

iii Pressurization with zero grade air to approximately 35 psig.

iv Venting to atmospheric pressure.

Step ii through iv are proceeded as a cycle. Recent experiments indicated that at most cases only three cycles are needed for the Canisters that have been used for two years. For relatively new Canisters even one cycle is adequate.

The Canisters for sampling should be at no more than 5 mm Hg vacuum.

V Blank test---is done by filling the Canisters with zero grade air through the cleaning system to a pressure of 15 psig approximately then analyzing the contents. Thus not only the Canisters but also the cleaning system is checked to prevent contamination. The results are compared with that from direct analysis of zero grade air.

b. Sampling---One canister collection sample at each site for every six days is requested. By the use of a metal bellows pump the ambient atmospheric air is drawn through a flow controller into the Canister. The pressure in the Canister usually reaches 15 psig over the sampling period of 24 hours.

c. Analysis of the Canister collection samples

i Apparatus being used:

Preconcentration trap : A laboratory-made trap, is fabricated from 1/8 inch (0.3175 cm) o.d., 0.21 cm i.d. chromatographic grade stainless steel tubing to suitable dimensions for a Dewar jar, a section of 5 inches (12 cm) long approx. the center is curled to a loop and packed with 60/80 mesh glass beads, which are held in place with dimethyl dichlorosilane-treated glass wool at both ends [16].

Ballast tank : A 1.2 liter volume, steel cylinder, fitted with an absolute pressure gauge, 0-400 mm Hg, by Wallace & Tiernan Co.

Gas chromatograph, and column : The same as that for the Tenax trap analytical system, except that about 15 cm of the beginning portion of the column is curled in a loop, which serves as a focusing trap, similar to Cryo-2 of the Tenax trap analytical system, 2.A.c.ii.(4)

Six port valves : 3 sets are employed:

V1--Shifting between VOC and NMOC analysis modes.

V2--Shifting between connection of the standard gas mixture and the Canister collected samples.

V3--Switches between sample loading into the cryo 1 and transfer of the pre-concentrated VOCs into the column.

Detectors : FID-A coupled with an ECD for VOC analysis, and FID-B alone for determination of None-Methane Organic Compounds (NMOC).

Recorder : 2-pen chart recorder, by Kipp & Zonen.

Utilities needed:

Carrier gas : Helium of zero grade, at 2 ml/min.

Make-up gas : Nitrogen of zero grade in two streams, one for the make-up of the capillary column effluent at 28 ml/min, the other for the ECD makeup at 27 ml/min.

Coolant : n-propanol slush at -100 °C to -120 °C for the preconcentration trap, and liquid nitrogen (-185 °C) for the focusing trap.

Split ratio of gas flow : ECD/FID = 1/10

It is worth taking notice that no gas dryers are employed. Though the EPA tested Nafion permeable membrane dryer as desirable [17], the experiments in the Air Pollution Research Laboratory led to contrary results and conclusions [14].

ii Analysis procedure

(1) Connecting and Heating---Attach the sampled Canister to the analytical system, which has been purged with zero grade nitrogen. The 1/8 inch o.d. stainless steel tubing for sample loading, and the six port valve V3 as well are heated to about 70 ^{o}C to prevent adsorption of the VOCs on the internal surface of the tubing, while the Canister is kept at 40 ^{o}C approximately to aid volatilization of the VOC contents.

(2) Sample loading---The air sample is loaded through the system into the ballast by a driving force resulted from the pressure difference between the pressure in the Canister (15 psig normally) and that in the ballast (less than 5 mm Hg). While being drawn through the system, the analytes in the sample are condensed in the preconcentration trap, which has been cooled by being immersed in a cold bath of n-propanol slush at -100 to -120 ^{o}C.

Sample loading is terminated when the ballast is filled with the VOC condensed-off sample up to certain pressure. This pressure should range from 5 to 8 psig to suit samples of different humidity. For lower humidity samples taken under dry & cool weather, more pressure is acceptable. For samples from humid air, a lower pressure is preferred, giving a smaller sample, so as to circumvent the water plugging problem in the GC column.

The pressure is used in the equation for sample volume calculation [14] :

$$V_a = \frac{\triangle P \times V_b}{P_a}$$

where:

$\triangle P$--Pressure difference said above, psi.

V_b---Volume of the ballast, 1.2 L.

P_a---Atmospheric pressure, 14.7 psi.

V_a---Sample volume equivalent to air volume under atmospheric condition, Liter.

(3) Transfer---The condensed VOCs are transferred by replacing the slush bath with boiling water, thus vaporizing the sample from the preconcentration trap to the focusing trap; which is placed in a cold bath of liquid N_2, through a transfer line of 1/16 inch o.d. stainless steel tubing heated at 60-80 ^{o}C. Six to eight min. is needed for the transfer [14], yet eight min. or longer is usually spent to better ensure complete transfer.

(4) Injection---The recondensed VOCs in the focusing trap are revolatilized by submerging the trap in another boiling water cup, and so injected onto the GC analytical column.

The column temperature is then controlled by a manually adjusted program : 35 ^{o}C initially for 8 min., then rising at a gradient of 6^{o}C/min to 83^{o}C, then changed to another gradient of 10 ^{o}C/min. to 153 ^{o}C, then 16^{o}C/min. to 195 ^{o}C, and kept for 5 min. The multi-stage temperature program enables best resolution. At the beginning 6^{o}C per min. is suitable for compounds that are eluted at temperatures lower than 80^{o}C; namely, MECL, DCM, C6, CFOR, 111, BZ, CCl4 and TRIC, in the elution sequence. However, 10 ^{o}C/min. gives better resolution for heavier compounds; TOL, PERC, MPX and OX. All the target compounds are eluted before the column temperature reaches 150 ^{o}C.

Then a gradient of 16 ^{o}C/min. is used simply to save time in reaching the final temperature 195 ^{o}C, which is considered necessary to elute any residue of the preceeding analytes.

d. Result generation: Integrations of peak areas and calculations of concentrations are done in the same manner as that for the Tenax trap method, stated in 2.A.d. Instead of relative response factors (RRF) of each target compounds normalized to the benzene calibration factor [17], the direct ratioing of peak areas of sample to that of the standard gas mixture is used in this project for calculations of concentrations.

The ration is as follows:

$$\frac{N_{I\text{-}sam}}{A_{I\text{-}sam}} = \frac{N_{I\text{-}std}}{A_{I\text{-}std}} \qquad (1)$$

$N_{I\text{-}sam}$ = Moles of I in the sample,

$N_{I\text{-}std}$ = Moles of I in the standard gas,

$A_{I\text{-}sam}$ = Peak area of I of the sample, and

$A_{I\text{-}std}$ = Peak area of I of the standard.

Since, $N = \frac{PV}{RT}$ then Equation (1) becomes:

$$\frac{V_{I\text{-}sam}}{A_{I\text{-}sam} \times T_{sam}} = \frac{V_{I\text{-}std}}{A_{I\text{-}std} \times T_{std}} \qquad (2)$$

$V_{I\text{-}sam}$ = Volume of I in the sample,

$V_{I\text{-}std}$ = Volume of I in the standard gas,

V_{sam} = Total sample volume,

V_{std} = Total standard gas volume,

$C_{I\text{-}sam}$ = Concentration of I of the sample, and

$C_{I\text{-}std}$ = Concentration of I of the standard gas.

$$C_{I\text{-}sam} = \frac{V_{I\text{-}sam}}{V_{sam}} \quad \& \quad C_{I\text{-}std} = \frac{V_{I\text{-}std}}{V_{std}}$$

$$\frac{C_{I\text{-}sam} \times V_{sam}}{A_{I\text{-}sam} \times T_{sam}} = \frac{C_{I\text{-}std} \times V_{std}}{A_{I\text{-}std} \times T_{std}} \tag{3}$$

Therefore;

$$C_{I\text{-}sam} = \frac{C_{I\text{-}std} \times A_{I\text{-}sam} \times V_{std} \times T_{sam}}{A_{I\text{-}std} \times V_{sam} \times T_{std}} \tag{4}$$

Where; $T_{sam} = 298^{o}K$, $T_{std} = 436^{o}K$.

Table 2.01 Characteristics of Tenax [11] [13]

Composition : (2,6-diphenyl-p-phenylene oxide)$_n$

Shape : Spherical

Diameter : 0.018-0.025 cm (0.007-0.0098 inches)

Mesh size : 60/80

Conditioning : Extraction with solvents and then drying

Desorption temperature : 250 °C

Temperature limit in use : 375 °C

Specific surface area : 35 m^2/g

Pore volume : 2.4 m^3/g

Average pore radius : 200 nm

Density : 0.16 g/cm^3

Structure :

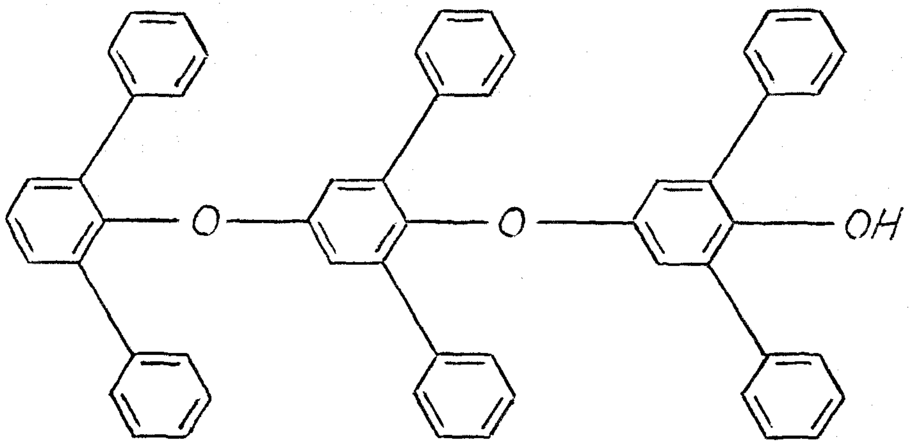


Table 2.02 EPA tested organic compounds using SUMMA polished canister

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)
Freon 12 (Dichlorodifluoromethane)	Cl_2CF_2	120.91	-29.8	-158.0
Methyl chloride (Chloromethane)	CH_3Cl	50.49	-24.2	-97.1
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	170.93	4.1	-94.0
Vinyl chloride (Chloroethylene)	$CH_2{=}CHCl$	62.50	-13.4	-1538.0
Methyl bromide (Bromomethane)	CH_3Br	94.94	3.6	-93.6
Ethyl chloride (Chloroethane)	CH_3CH_2Cl	64.52	12.3	-136.4
Freon 11 (Trichlorofluoromethane)	CCl_3F	137.38	23.7	-111.0
Vinylidene chloride (1,1-Dichloroethene)	$C_2H_2Cl_2$	96.95	31.7	-122.5
Dichloromethane (Methylene chloride)	CH_2Cl_2	84.94	39.8	-95.1
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	187.38	47.7	-36.4
1,1-Dichloroethane (Ethylidene chloride)	CH_3CHCl_2	98.96	57.3	-97.0
cis-1,2-Dichloroethylene	$CHCl{=}CHCl$	96.94	60.3	-80.5
Chloroform (Trichloromethane)	$CHCl_3$	119.38	61.7	-63.5
1,2-Dichloroethane (Ethylene dichloride)	$ClCH_2CH_2Cl$	98.96	83.5	-35.3
Methyl chloroform (1,1,1-Trichloroethane)	CH_3CCl_3	133.41	74.1	-30.4
Benzene (Cyclohexatriene)	C_6H_6	78.12	80.1	5.5
Carbon tetrachloride (Tetrachloromethane)	CCl_4	153.82	76.5	-23.0
1,2-Dichloropropane (Propylene dichloride)	$CH_3CHClCH_2Cl$	112.99	96.4	-100.4
Trichloroethylene (Trichloroethene)	$ClCH{=}CCl_2$	131.29	87	-73.0
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$CH_3CCl{=}CHCl$	110.97	76	

Table 2.02 (cont'd)

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT(°C)	MELTING POINT (°C)
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	$ClCH_2CH=CHCl$	110.97	112.0	
1,1,2-Trichloroethane (Vinyl trichloride)	$CH_2ClCHCl_2$	133.41	113.8	-36.5
Toluene (Methyl benzene)	$C_6H_5CH_3$	92.15	110.6	-95.0
1,2-Dibromoethane (Ethylene dibromide)	$BrCH_2CH_2Br$	187.88	131.3	9.8
Tetrachloroethylene (Perchloroethylene)	$Cl_2C=CCl_2$	165.83	121.1	-19.0
Chlorobenzene (Phenyl chloride)	C_6H_5Cl	112.56	132.0	-45.6
Ethylbenzene	$C_6H_5C_2H_5$	106.17	136.2	-95.0
m-Xylene (1,3-Dimethylbenzene)	1,3-$(CH_3)_2C_6H_4$	106.17	139.1	-47.9
p-Xylene (1,4-Dimethylxylene)	1,4-$(CH_3)_2C_6H_4$	106.17	138.3	13.3
Styrene (Vinyl benzene)	$C_6H_5CH=CH_2$	104.16	145.2	-30.6
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167.85	146.2	-36.0
o-Xylene (1,2-Dimethylbenzene)	1,2-$(CH_3)_2C_6H_4$	106.17	144.4	-25.2
1,3,5-Trimethylbenzene (Mesitylene)	1,3,5-$(CH_3)_3C_6H_6$	120.20	164.7	-44.7
1,2,4-Trimethylbenzene (Pseudocumene)	1,2,4-$(CH_3)_3C_6H_6$	120.20	169.3	-43.8
m-Dichlorobenzene (1,3-Dichlorobenzene)	1,3-$Cl_2C_6H_4$	147.01	173.0	-24.7
Benzyl chloride (α-Chlorotoluene)	$C_6H_5CH_2Cl$	126.59	179.3	-39.0
o-Dichlorobenzene (1,2-Dichlorobenzene)	1,2-$Cl_2C_6H_4$	147.01	180.5	-17.0
p-Dichlorobenzene (1,4-Dichlorobenzene)	1,4-$Cl_2C_6H_4$	147.01	174.0	53.1
1,2,4-Trichlorobenzene	1,2,4-$Cl_3C_6H_3$	181.45	213.5	17.0
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)				

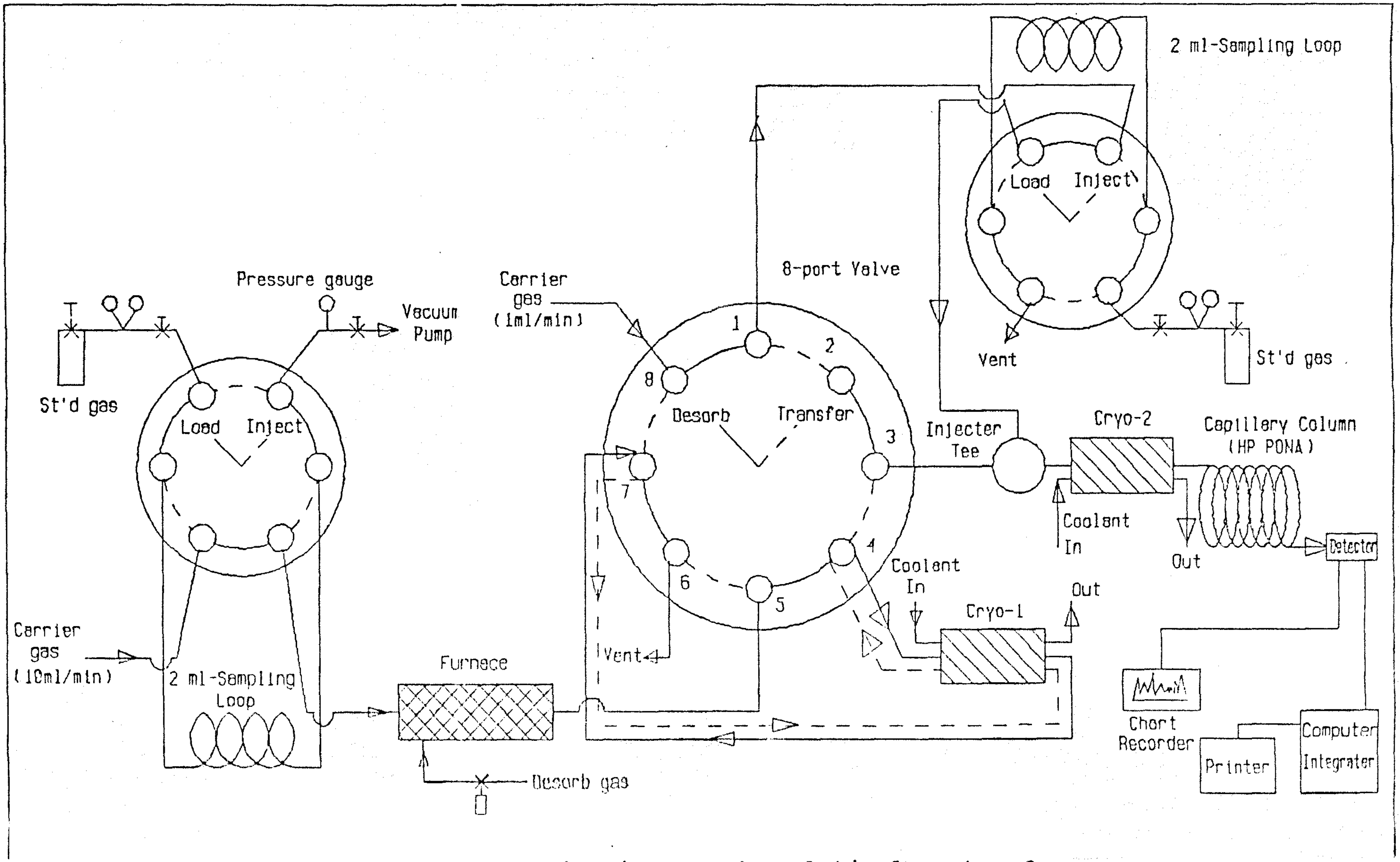


Figure 2.01 Schematic diagram of analytical system for the Tenax trap method

Figure 2.02 Schematic diagram of cleaning system for Canister collection method

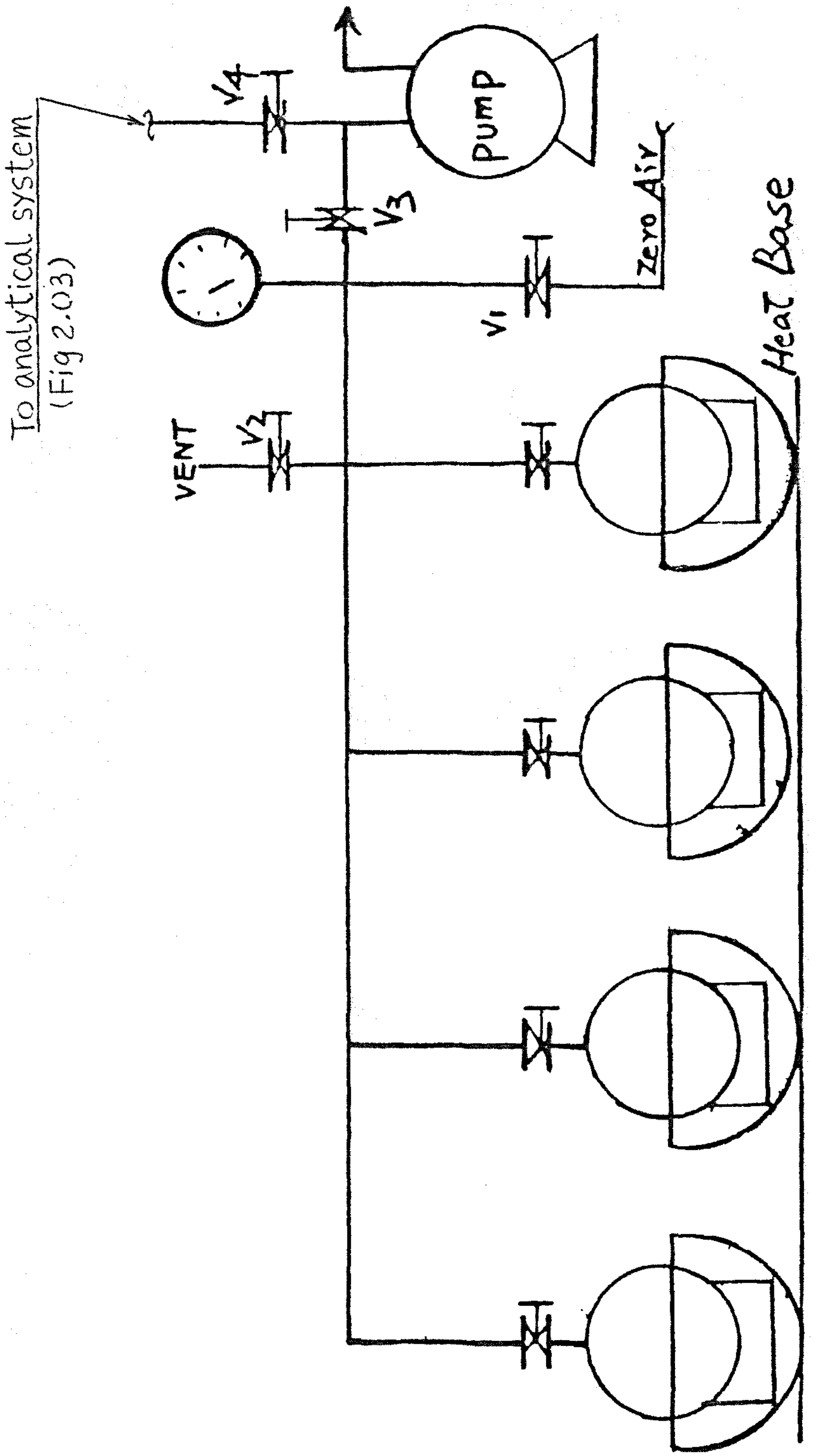
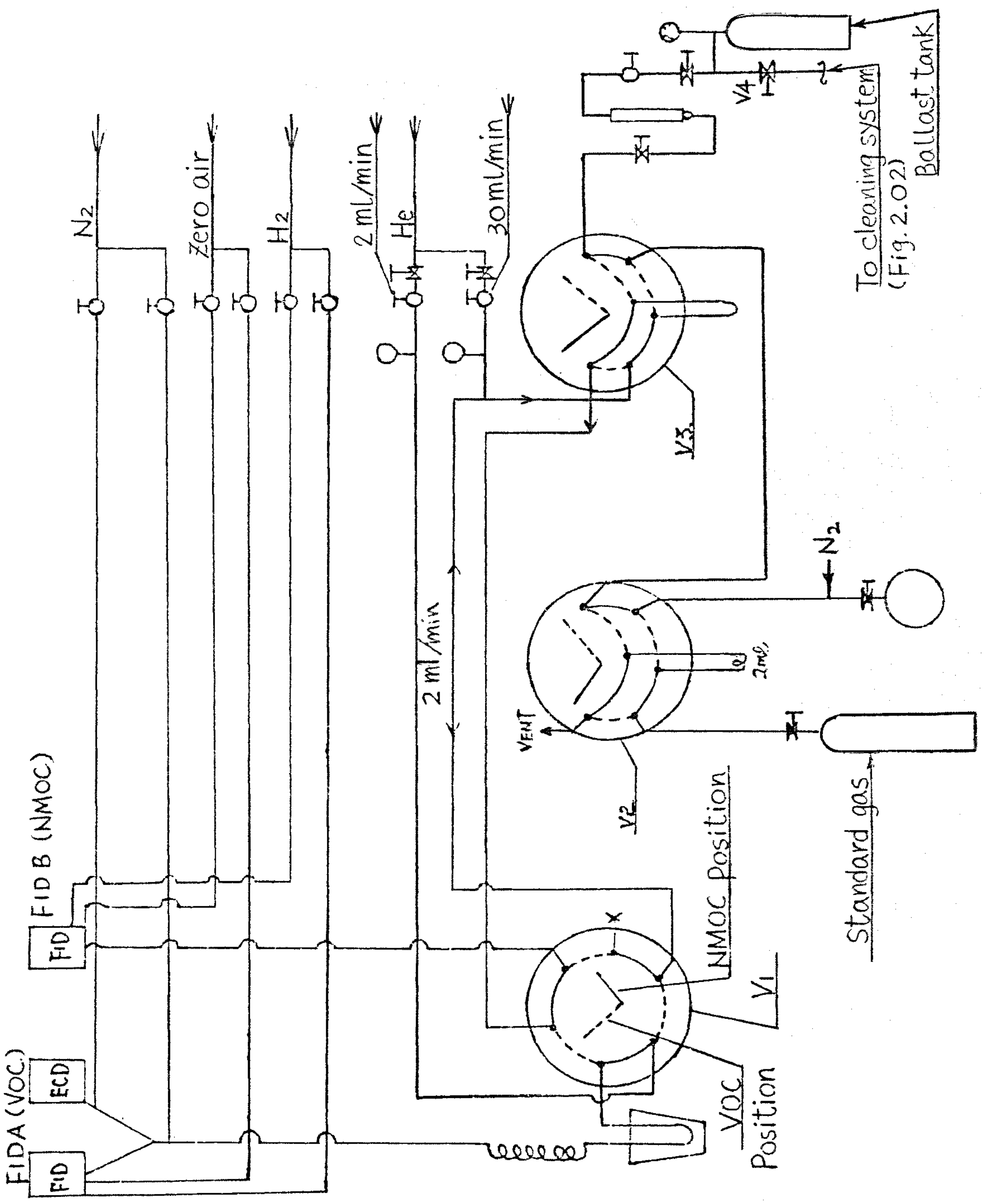


Figure 2.03 Schematic diagram of analytical system for Canister collection method



3. DEVELOPMENT HISTORY OF THE TWO SYSTEMS IN THE AIR POLLUTION RESEARCH LABORATORY

Both the Tenax trap and the Canister collection systems in the laboratory have been changed individually since they were established. They are related chronologically below, and the improvements resulting from the changes are subsequently defined.

A. Changes on the Tenax trap system

According to the protocol of the project, spiked samples are periodically delivered from the EPA to the laboratory for the purpose of quality assurance.

For the first two spikes in June, 87 and November, 87, the results from the Tenax trap system consistently showed negative bias in every target compound.

Table 3.01 presents a contrast of detected amounts against the spiked nanograms of each compound in the spike of November, 87. The differences between the reported and the spiked narograms range from -58 % (111*) to -79 % (PERC), indicating that severe loss of each compound occurred. The causes were eventually traced after thorough examination and the solutions to the problems are described as follows:

a. Cold spots---during the transfer, certain points in the transfer line of the Tekmar desorber, adjacent to the coolant inlet to the eight-port valve, were found to remain cold enough to prevent the vaporized VOCs from transfering.

After a heating device was fitted onto the locations, the recovery rates for all compounds were considerably enhanced.

b. Shortening the Tenax packing section

Another reason for losses of the compounds was that during the prepurge, when a trap was placed in the desorber furnace, the lower part of the Tenax-packed section, which contacted a heat source in the desorber, was actually heated near 80 ^{o}C by thermoconductivity through the stainless steel tube wall, though the prepurge temperature was set at and displayed 40^{o}C. It turned out that part of the analyte was unexpectedly desorbed and purged away.

To correct this, the packed section was shortened from about 14 cm to 6 cm, and was located at the upper part of the tube, leaving the lower part empty. The amount of packed Tenax was consequently reduced from 500 mg to 350 mg, and the sampling volumes for high and low duplicate traps were also decreasd from 28 and 14 liters to 14 and 7 liters respectively.

Statistical data analyses were done for the concentrations of the samples collected before and after shortening the packing bed, 12 samples in each group.

Table 3.02 and 3.03 show the comparison.

The results are as follows:

i For every compound, the deviation of low and high flow traps before the change are more random and more scattered.

ii The sums of deviations of low-high flow traps before the use of the shorter packing bed are typically less than after the use, due to the fact that positive and negative deviations countervail each other.

iii However, the absolute sums of deviations are significantly decreased for compounds; C6, 111*, CCL4, TOL, PERC, PMX, AND OX. Upon the theory that breakthrough is definitely more obvious in high flow trap than in the low , that implies that since the positive deviations obtained from the samples in old traps are regarded as results of system uncertainty, the decrease of absolute sums of the deviations is an indication of better reliability in the shorter traps.

iv As for the averages of 12 samples, before the change the average is higher than that after, typically for all the compounds. The explanation for this finding is the samples collected in the old traps were from winter atmospheric ambient air, while those in the new traps are coincidently from warmer spring season. It is known that concentrations of air pollutants are normally higher in winter since the inversion layer of the atmosphere is lower than that in summer.

c. ECD peak area calibration

Co-elution of some chloro-compounds was first revealed by GC-MS analysis and further confirmed by peak ratioing of FID and ECD peaks [13]. Figures 3.01 through 3.03 present a typical example of such. Part A of Figure 3.01 shows total ion chromatogram (TIC) of a sample collected at the Elizabeth site on July 6, 89. The marked peak appears as a whole one, yet the enlargement of it shows that it is two as shown in Part B.

Figures 3.02 and 3.03 show the mass spectra of co-eluted hydrocarbon and perchloroethene (PERC), which is one of the target compounds. Another example of co-elution of BZ and CCL4 is additionally given in Figure 3.04 as a reference, though it is not from any sample of the project. In such cases, the peaks are too close to be separated by the computer software package program, thus yielded erroneous peak areas and consequently led to unreasonably high concentrations.

ECD peak area calibration was initiated in February, 88 on the Tenax trap system for chlorides, CFOR, 111*, CCL4, TRIC, and PERC. As for MECL and DCM, they remain quantitated by the FID, because the ECD does not respond to these two compounds.

After all these modifications, the Tenax trap system was much improved, which can be evidenced by the results of the EPA spiked sample processed in June, 88, as shown in Part A of Table 3.04. The differences between the detected amounts and the spiked are in a range of -7.8 % to 57.33, and the average bias is 23.19 %.

B. Changes on the Canister collection system

The system was first set up with FID, later coupled with an ECD in August, 87. Since then a series of modifications have been made and much improvement was achieved.

a. Change of cold bath to n-propanol slush

Before the change, the cold bath for the preconcentration trap had been using liquid argon, as recommended by the EPA [16]. The carbon dioxide collected in the Canisters always imposed an effect in the GC column, which broadened many peaks of earlier part of the chromatogram. Started in March, 88, a new cold bath of n-propanol slush was used. This is made by mixing liquid nitrogen into n-propanol container, until a temperature of around -110 ^{o}C is obtained. The use of a cold bath at -110 ^{o}C rather than -180 ^{o}C of liquid argon helps to circumvent the carbon dioxide problem, because the carbon dioxide in the sample is not trapped at -110 ^{o}C, instead, is passed away to the ballast tank, which is beyond the sample loading system.

The improvement in column resolution is obvious and impressive as seen in Figures 3.05 to 3.08. Both the standard gas mixture with addition of 0.5 ml CO_2 and a regular sample were analyzed twice, one by use of liquid argon at the preconcentration trap, the other by n-propanol slush.

These experiments ascertained the reason of poor resolution of the chromatograms when using liqid argon as a cold bath is the carbon dioxide in the sample, rather than the water vapor, as had been suspected.

b. ECD Peak height calibration

Since the co-elution of some target chlorides and hydrocarbons in FID chromatogram was ascertained, calibration by ECD response became a necessity. An additional data acquisition channel in the A/D conversion hardware was set up in October, 88, for ECD peak area integration. Before that time, only ECD chromatograms were available without integration. Figures 3.09 to 3.13 present calibration curves of concentration versus ECD peak heights for chlorides, CFOR, 111*, CCL4, TRIC, and PERC. The curves show fairly good regressions, with variances range from -1.658 x 10^{-5} to -6.654 x 10^{-5}. This fact confirms the report that for certain chlorides more repeatable results can be obtained by measurement of ECD peak heights on the integrator trace rather than relying on the electronically integrated peak areas on the FID channel alone[21].

c. ECD Peak area calibration

Automatic integration of ECD peak areas has been used for calibration of the five chlorides above, since the necessary hardware assembly and the calibration curves were carried out. The equations for calibration are as follows:

Y---Concentration in ppb,

X---Peak area in various denominators.

CFOR, $Y = -0.001336 + 0.2486X + 0.04788X^2$

X = Peak area/500

111*, $Y = 0.01686 + 0.5281X + 0.2251X^2$

X = Peak area/1800

CCL4, $Y = 0.0001577 + 0.522X + 0.02211X^2$

X = Peak area/6000

TRIC, $Y = 0.005214 + 0.4779X + 0.05653X^2$

X = Peak area/1200

PERC, $Y = -0.0006419 + 0.1701X + 0.1289X^2$

X = Peak area/4000

After the modifications above, the performance of the Canister system was greatly upgraded. Table 3.04 Part B indicates the results of the EPA spiked sample of June, 88. The deviations range from -51 % to 40 %, and the average deviation is -6.32 %.

Table 3.01 Results of spiked sample for Tenax trap system

November, 1987

	Spiked, ng		Reported, ng		Difference, %	
Compound	Trap # 120	122	120	122	120	122
CFOR	54	108	15	45	-72	-58
111*	121	243	51	112	-58	-54
CCL4	145	291	52	129	-64	-56
BZ	192	384	69	157	-64	-59
TRIC	213	426	49	159	-77	-63
TOL	220	441	50	137	-77	-69
PERC	177	354	37	119	-79	-66
OX	192	384	68	122	-65	-68

Average Loss--trap # 120, -69.5 %

trap # 122, -61.63 %

Table 3.02

Comparison of analytical results from the Tenax trap system before and after the use of shorter traps

(compounds; MECL, DCM, C6, 111*, & BZ)

Date	MECL		DCM		C6		111*		BZ	
	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A
12/05/87	0.01	0.00	0.01	0.00	0.10	-1.79	0.07	-1.71	0.26	-0.35
12/11	2.34	1.25	5.05	-0.05	2.29	-0.15	0.77	-0.36	3.20	0.05
12/17	2.78	1.19	4.03	-0.14	2.23	-0.25	0.77	-0.46	3.09	-0.04
12/23	0.01	0.00	1.01	1.98	2.33	0.04	0.61	0.08	2.83	0.00
12/29	0.01	0.00	0.01	0.00	0.12	-0.67	0.14	-0.96	0.43	-0.28
01/04	0.01	0.00	0.01	0.00	0.06	0.55	0.05	-1.56	0.17	-0.55
01/16	0.05	1.60	2.18	-0.28	1.71	0.73	0.48	0.99	1.35	0.47
01/22	0.11	0.48	0.01	0.00	0.48	-1.12	0.84	-0.14	0.95	-0.76
01/28	0.03	-1.33	0.58	0.62	0.10	1.37	0.32	0.86	0.31	1.29
02/03	0.26	0.90	0.48	0.65	0.08	0.93	2.44	0.85	0.70	1.02
02/09	0.01	0.00	0.01	0.00	0.24	-0.30	0.68	0.67	0.58	-0.16
02/15	0.01	0.00	0.01	0.00	1.58	0.11	1.44	-1.99	4.10	0.59
Avg	0.47	0.34	1.11	0.23	0.94	-0.04	0.71	-0.31	1.50	0.11
Sum		4.09		2.78		-0.53		-3.74		1.29
Abs Sum		6.75		3.72		7.99		10.64		5.57

	MECL		DCM		C6		111*		BZ	
	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A
03/04	0.24	0.72	2.66	0.33	0.86	0.33	1.62	0.49	1.16	0.34
03/10	0.10	0.80	0.39	-0.92	0.25	0.24	2.53	1.62	0.53	0.45
03/16	0.13	0.62	0.01	0.00	0.30	0.27	0.37	0.52	0.44	0.27
03/22	0.07	0.29	3.87	0.18	1.18	0.29	0.95	0.35	1.34	0.34
03/28	0.11	0.73	1.30	0.28	0.60	0.33	0.47	0.26	0.72	0.31
04/03	0.20	1.00	0.94	0.66	0.46	0.33	0.71	0.73	0.64	0.46
04/09	0.09	0.22	0.30	0.20	0.20	0.36	0.17	0.30	0.62	0.34
04/21	0.23	0.17	0.71	0.35	0.31	0.39	0.22	0.09	0.43	0.68
04/27	0.01	0.00	0.38	0.13	0.30	-0.07	0.45	0.36	0.51	0.16
05/03	0.26	0.85	1.02	0.21	0.82	0.20	1.05	0.30	1.17	0.23
05/09	0.21	0.63	0.26	0.82	0.12	0.50	0.34	0.21	0.41	0.44
05/15	0.01	0.00	0.01	0.00	0.17	-0.06	0.58	0.85	0.49	0.53
Avg	0.14	0.50	0.99	0.19	0.46	0.26	0.79	0.51	0.70	0.38
Sum		6.03		2.24		3.10		6.08		4.56
Abs Sum		6.03		4.08		3.36		6.08		4.56

Table 3.03

Comparison of analytical results from the Tenax trap system before and after the use of shorter traps

(compounds; CCL4, TRIC, TOL, PERC, PMX & OX)

Date	CCl4		TRIC		TOL		PERC		PMX		OX	
	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A
12/05/87	0.10	0.00	0.01	0.00	0.37	-0.65	0.01	0.00	0.08	-0.25	0.02	-1.00
12/11	2.92	0.12	1.01	-0.23	9.14	-0.33	0.36	-0.42	2.53	-0.66	0.73	-0.77
12/17	1.94	0.02	1.00	-0.05	8.53	-0.42	0.33	-0.55	2.35	-0.74	0.68	-0.84
12/23	1.09	0.78	0.01	0.00	6.87	0.31	0.29	-0.88	2.29	0.07	0.90	0.09
12/29	0.09	-0.82	0.01	0.00	0.70	-0.31	0.09	-1.33	0.25	0.96	0.08	0.40
01/04	0.10	0.00	0.03	1.20	0.27	-0.72	0.03	0.40	0.13	-0.72	0.07	-0.77
01/16	0.12	0.33	0.11	-1.82	3.17	0.03	0.50	-0.68	0.93	0.49	0.32	0.79
01/22	0.60	-0.50	0.01	0.00	2.04	-1.16	0.15	-0.34	0.63	-1.14	0.24	-1.06
01/28	0.35	0.74	0.01	0.00	0.67	1.55	0.10	1.60	0.30	1.66	0.15	1.47
02/03	0.53	1.02	0.01	0.00	0.22	0.91	0.05	0.67	0.12	1.48	0.07	1.08
02/09	0.73	0.99	0.01	0.00	1.49	-0.28	0.17	1.03	0.54	-0.17	0.23	0.13
02/15	1.21	-1.83	0.01	0.00	12.35	-0.98	0.01	0.00	8.49	-1.37	2.81	-1.39
Avg	0.81	0.07	0.18	-0.07	3.82	-0.17	0.17	-0.04	1.55	-0.03	0.52	-0.16
Sum		0.85		-0.90		-2.06		-0.51		-0.38		-1.87
Abs Sum		7.15		3.30		7.66		7.91		9.70		9.79

	CCl4		TRIC		TOL		PERC		PMX		OX	
	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A	Avg	L-H/A
03/04	0.90	0.56	0.36	-0.06	3.23	0.35	0.30	0.37	1.20	0.37	0.45	0.47
03/10	1.47	1.04	0.15	0.48	1.11	0.37	0.15	-0.48	0.44	0.39	0.18	0.40
03/16	0.99	0.75	0.01	0.00	0.95	0.29	0.12	0.61	0.33	0.30	0.14	0.37
03/22	1.26	0.37	0.16	0.45	4.21	0.29	0.57	0.56	1.28	0.31	0.46	0.24
03/28	0.20	0.50	0.09	0.67	2.12	0.28	0.28	0.21	0.69	0.26	0.27	0.37
04/03	0.21	0.63	0.08	0.50	1.52	0.42	0.42	0.36	0.53	0.40	0.20	1.00
04/09	0.18	0.29	0.03	0.40	0.30	0.27	0.09	0.35	0.30	0.27	0.09	0.22
04/21	0.10	0.00	0.05	1.11	0.78	1.74	0.03	1.33	0.27	1.92	0.23	-0.17
04/27	0.21	0.24	0.05	0.67	1.19	0.12	0.32	0.54	0.45	0.29	0.24	0.55
05/03	0.21	0.24	0.09	0.35	4.03	0.22	0.48	0.46	0.41	0.17	1.11	0.21
05/09	0.30	0.40	0.04	-0.29	1.16	0.25	0.33	0.42	0.16	0.25	0.36	0.25
05/15	0.65	0.52	0.01	0.00	0.80	0.28	0.36	0.22	0.28	0.69	0.31	0.19
Avg	0.55	0.46	0.09	0.36	1.78	0.40	0.29	0.41	0.53	0.47	0.33	0.34
Sum		5.54		4.29		4.85		4.97		5.62		4.11
Abs Sum		5.54		4.99		4.85		5.93		5.62		4.45

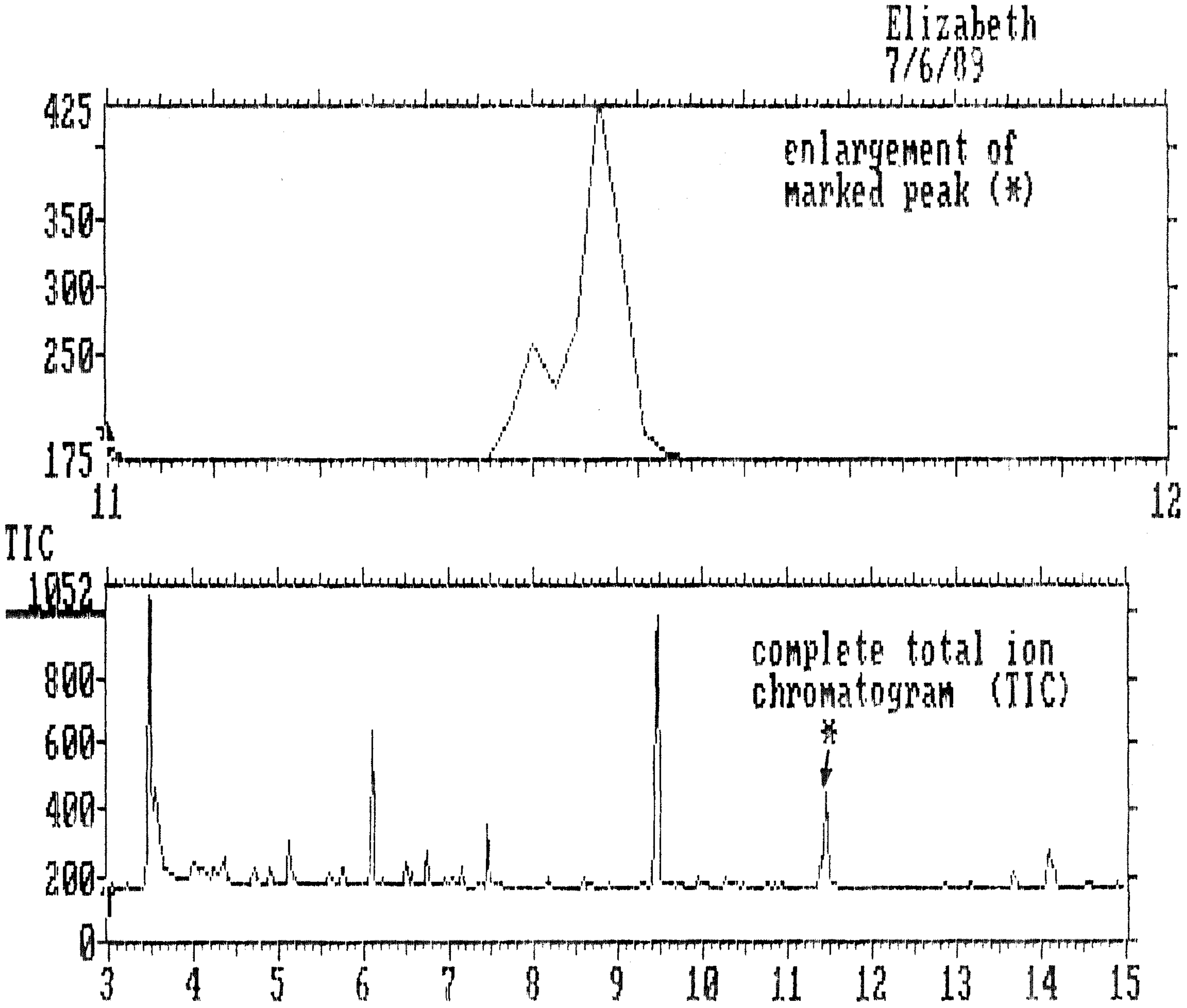
Table 3.04 Results of spiked samples for the two systems June, 1988

Part A----Tenax trap system

Compound	Trap #	Spiked, ng			Reported, ng			Average Bias, %
		103	109	110	103	109	110	
CFOR		72	72	108	79	85	134	17.23
111*		97	97	146	97	103	146	2.07
BZ		128	128	192	155	155	226	20.0
CCL4		116	116	174	163	167	246	41.67
TRIC		142	142	213	175	176	256	22.33
TOL		147	147	220	233	234	341	57.33
PERC		118	118	177	155	162	230	32.66
OX		128	128	192	118	118	177	-7.8
							Overall Average	23.19 %

Part B----Canister collection system

Compound	Spiked, ppb	Reported, ppb	Bias, %
DCM	4.6	3.4	-26
CFOR	4.8	4.1	-15
111*	4.7	6.6	40
BZ	4.3	4.0	-7.0
CCL4	4.6	4.4	-4.3
TRIC	5.6	5.4	-3.6
TOL	4.8	5.3	10.0
PERC	4.9	4.9	0
OX	4.9	2.4	-51.0
		Overall Average	-6.32 %



Part B

Part A

Figure 3.01 GC-MS Chromatogram of co-eluted peaks
(As courtesy from Dr. E Ritter)

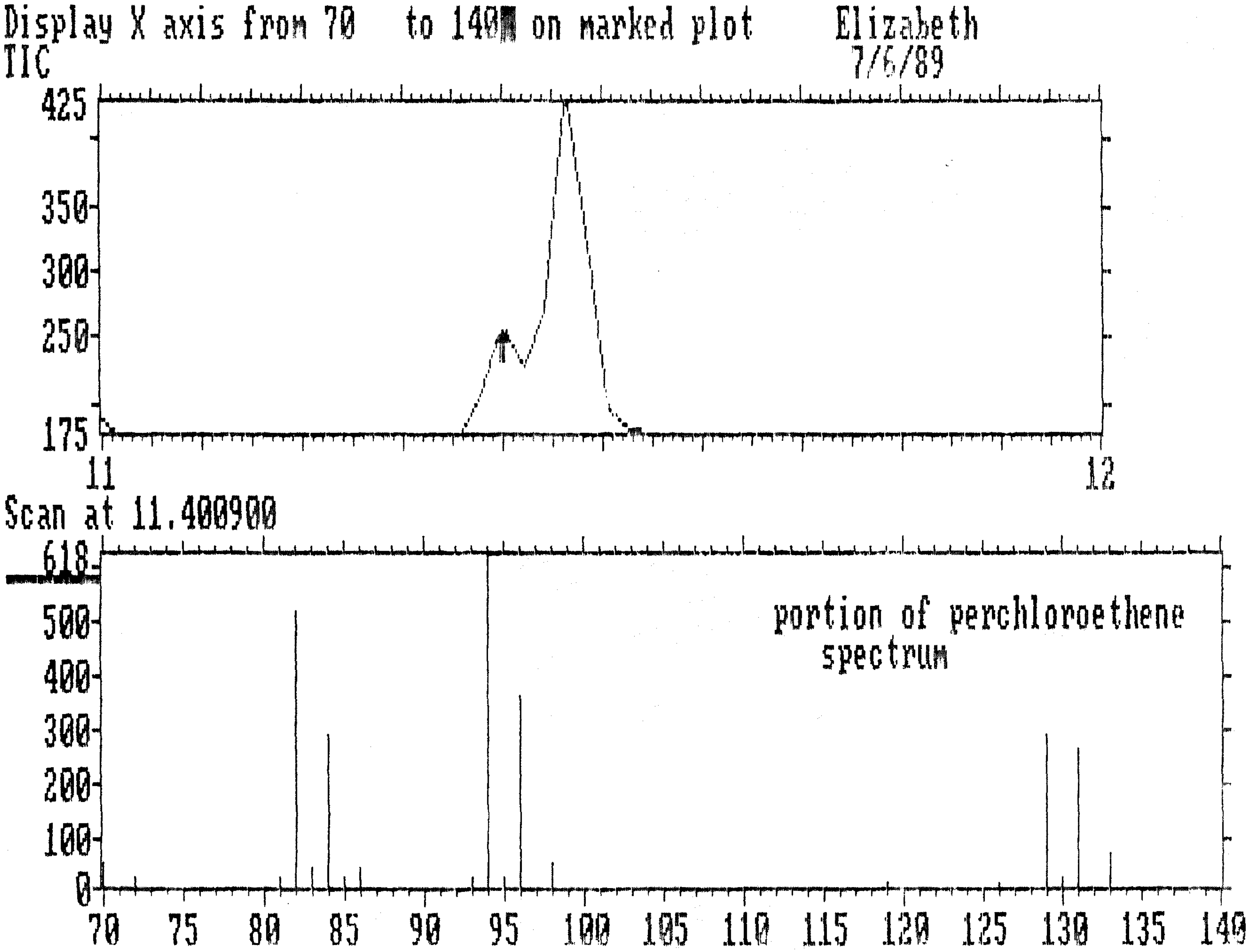
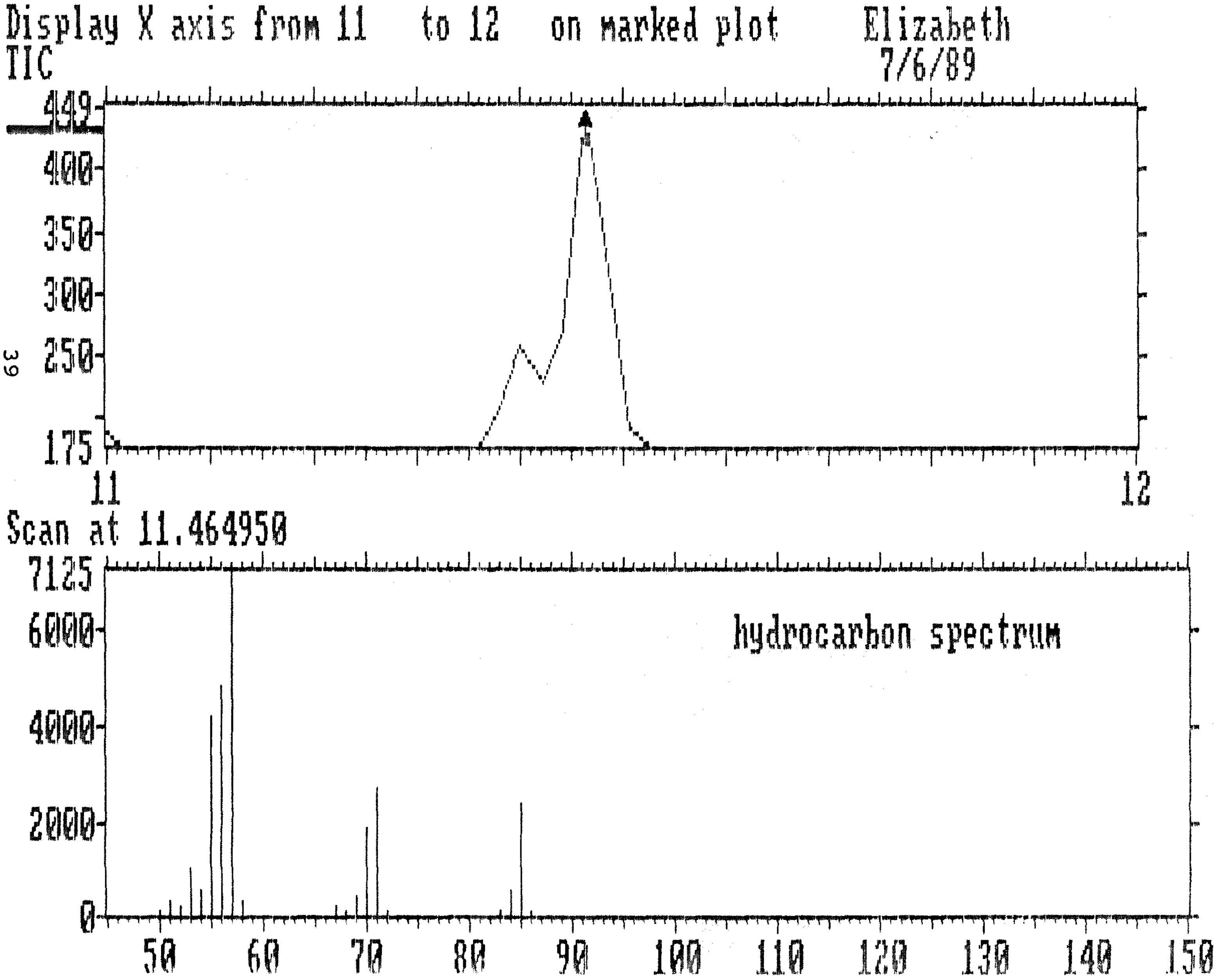


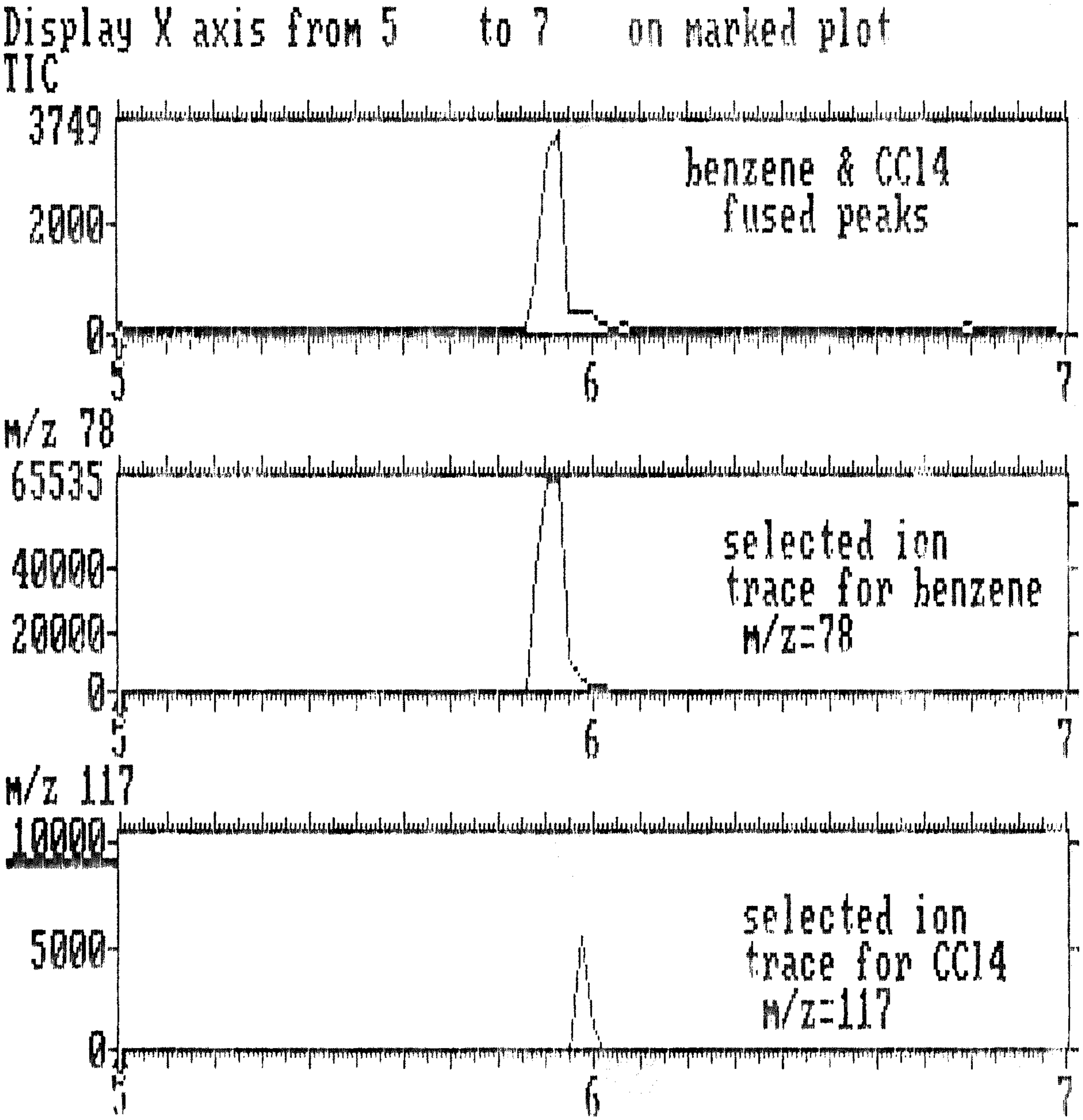
Figure 3.02 Gas chromatogram & MS spectrum (PERC)
(As courtesy from Dr. E Ritter)



Part B

Part A

Figure 3.03 Gas chromatogram & MS spectrum (hydrocarbon)
(As courtesy from Dr. E Ritter)



Part A

Part B

Part C

Figure 3.04 GC-MS Chromatogram of co-eluted peaks (BZ & CCL4)
(As courtesy from Dr. E. Ritter)

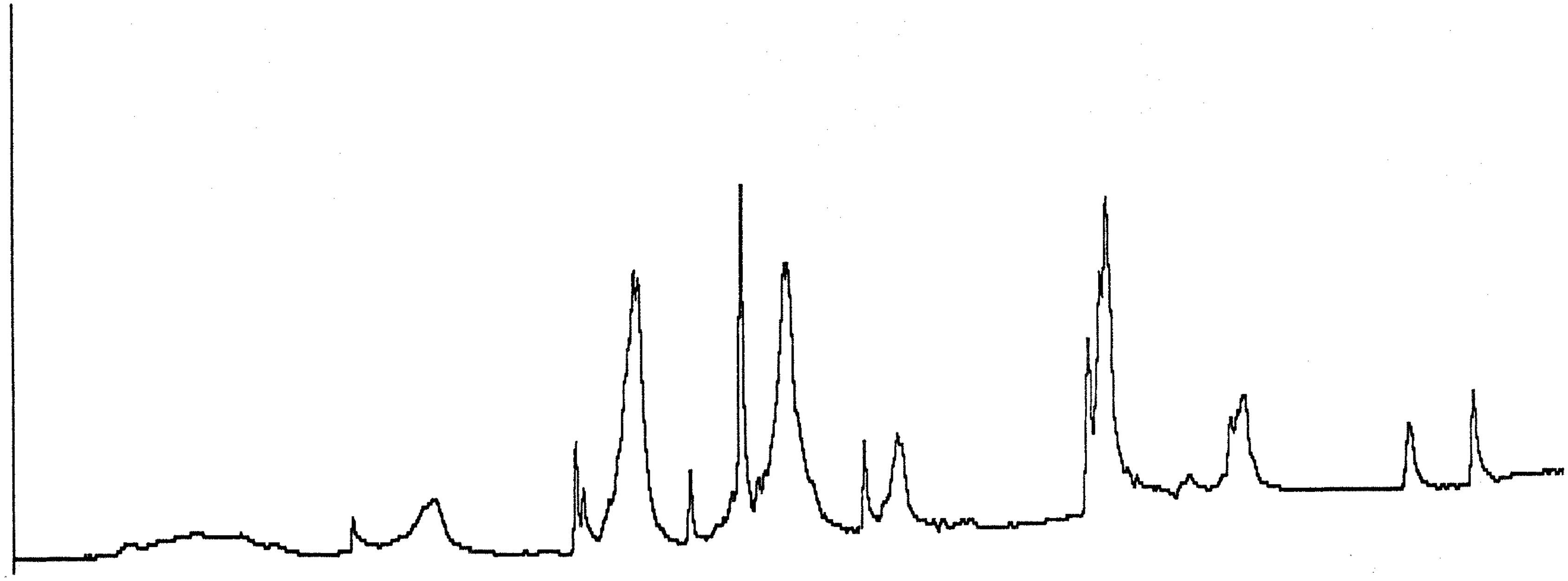


Figure 3.05 Chromatogram for analysis of standard gas mixture plus CO_2 with cold bath of liquid argon

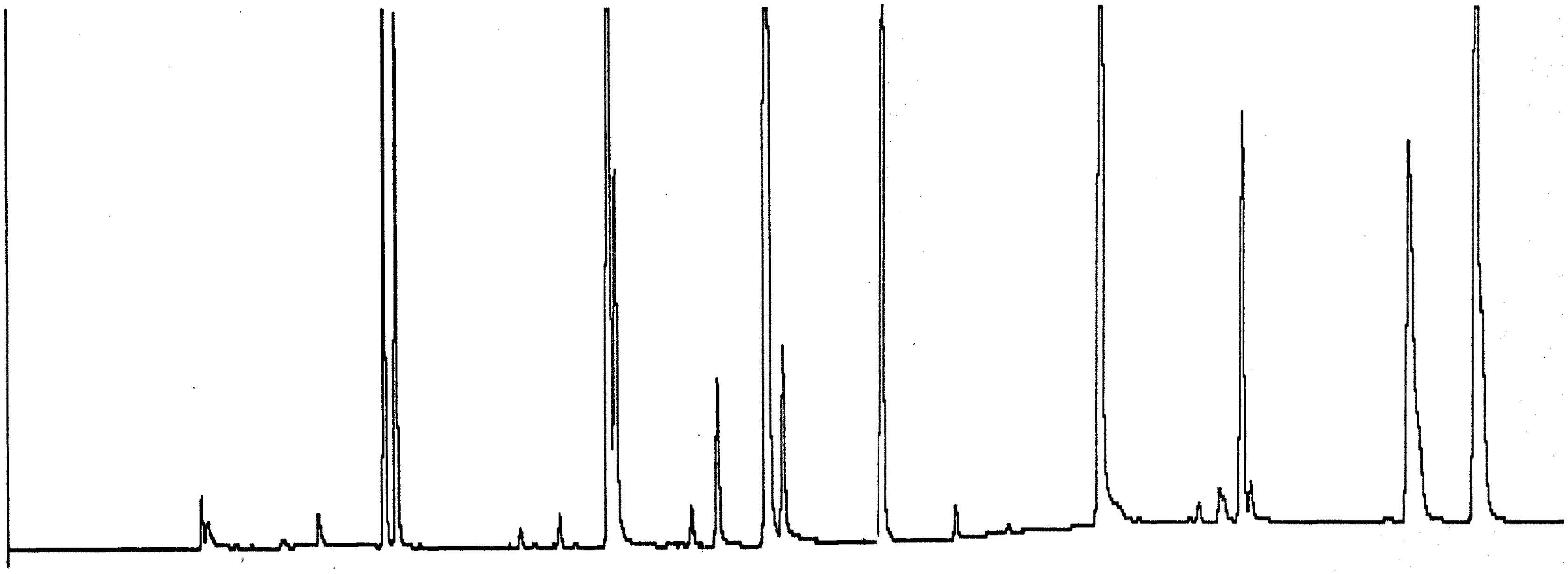


Figure 3.06 Chromatogram for analysis of standard gas mixture plus CO_2 with cold bath of n-propanol slush

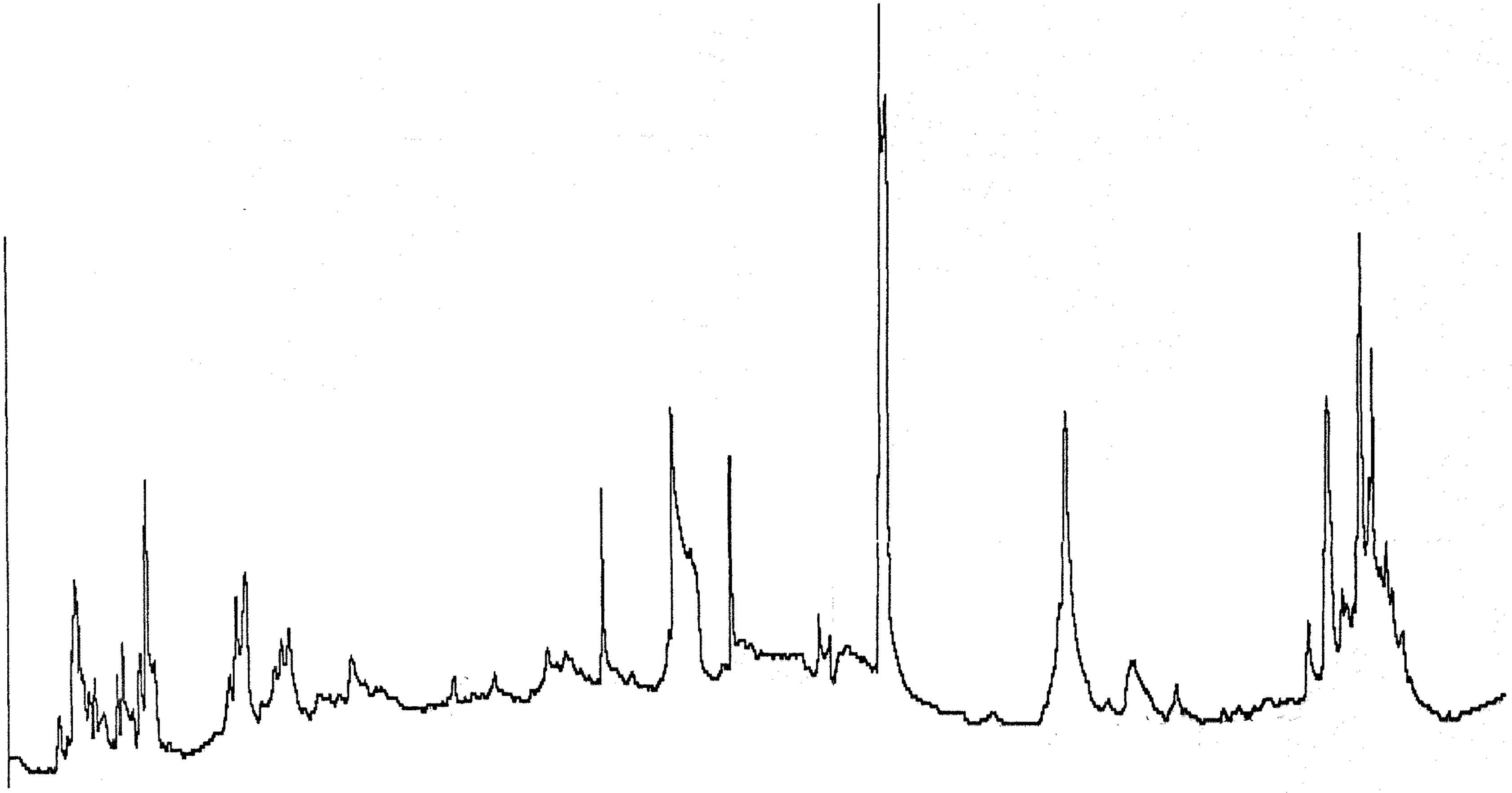


Figure 3.07 Chromatogram for analysis of regular sample with cold bath of liquid arrgon

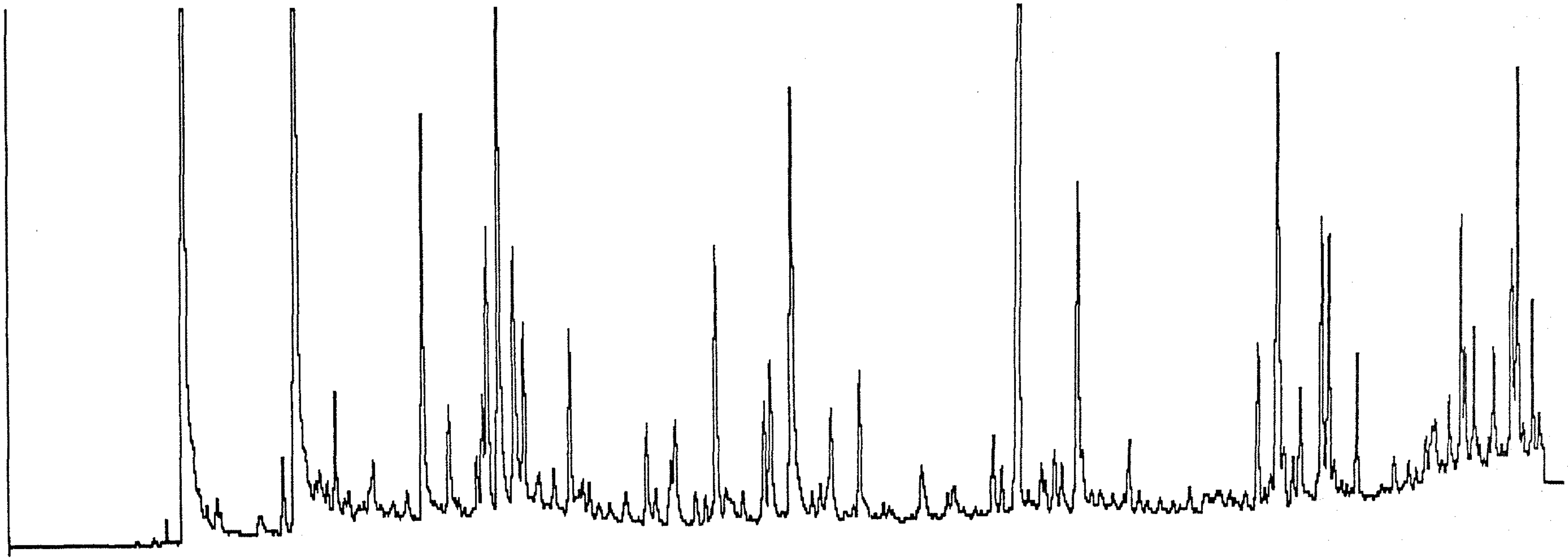
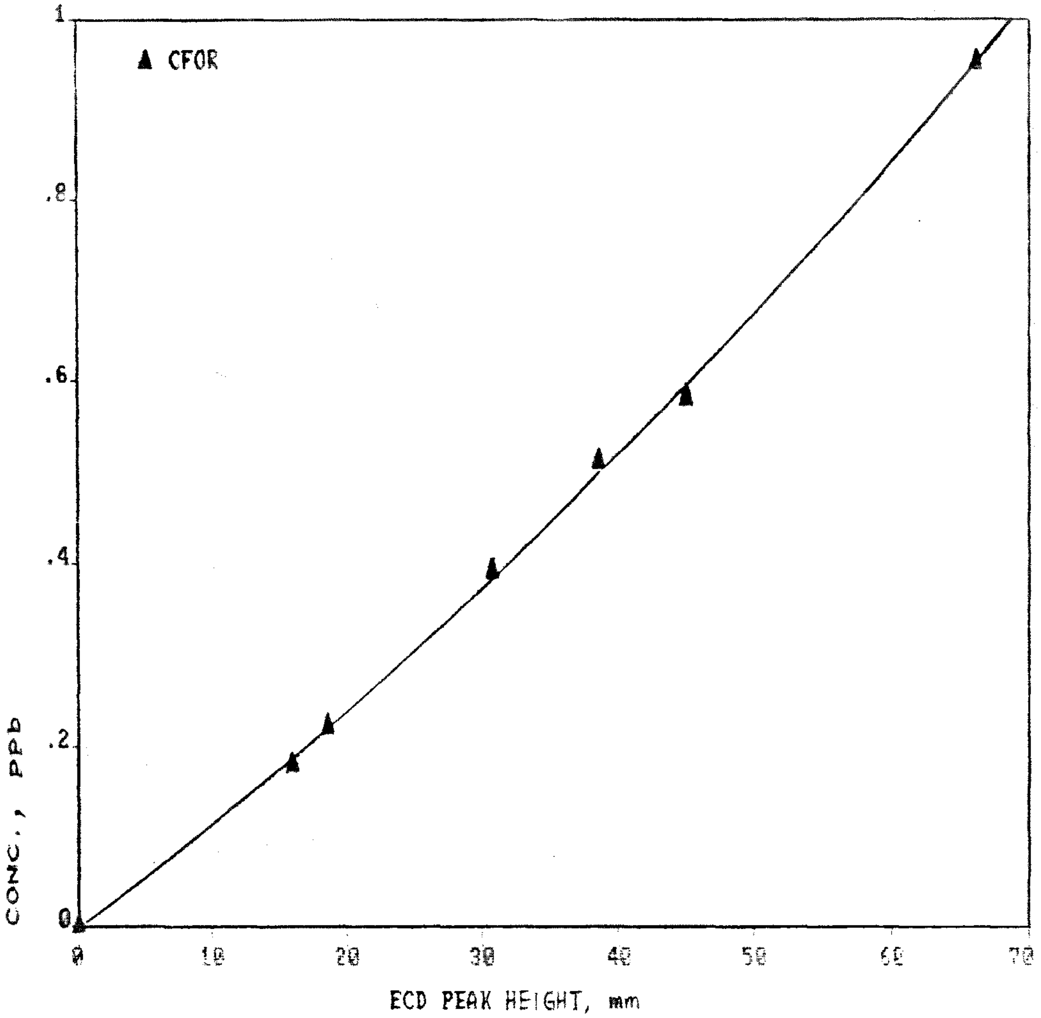


Figure 3.08 Chromatogram for analysis of regular sample with cold bath of n-propanol

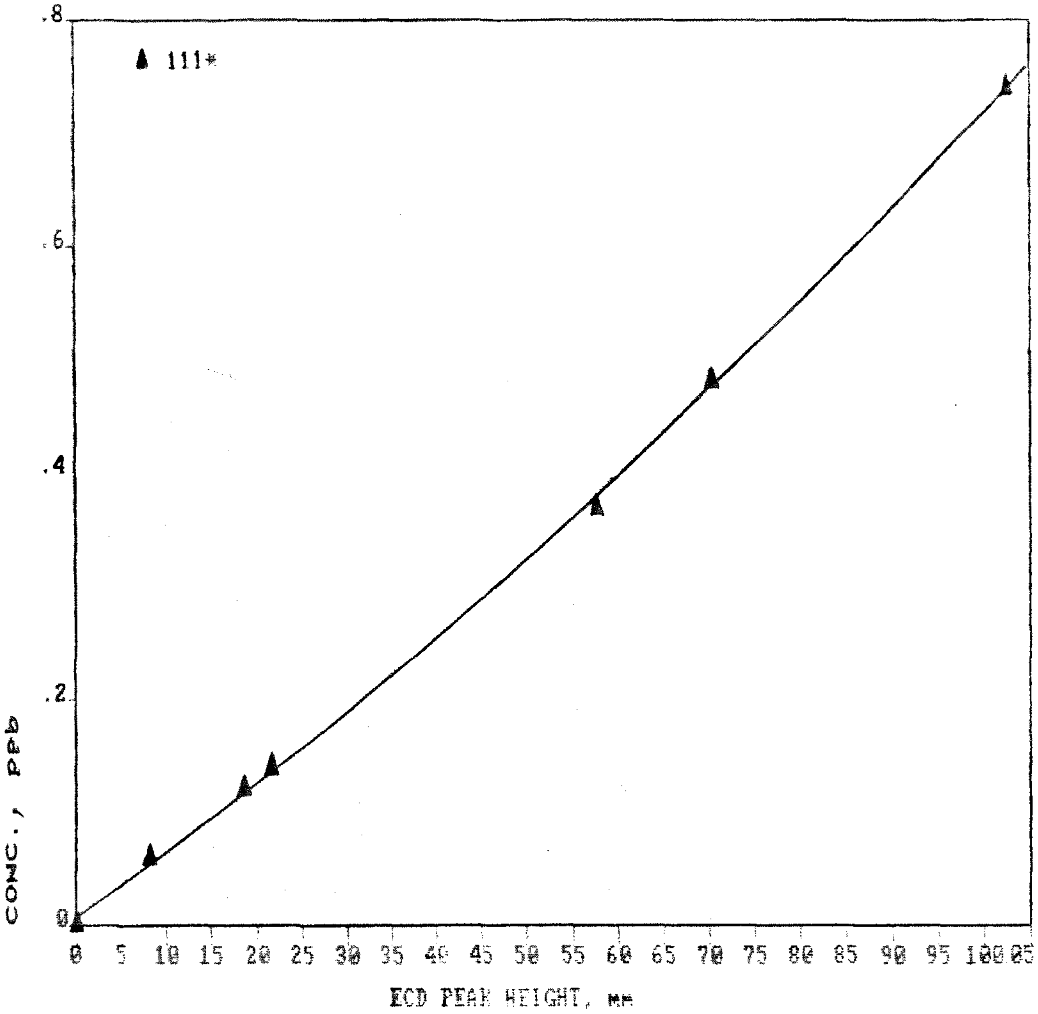
Figure 3.09 Calibration with ECD peak height fot CFOR



THE REGRESSION POLYNOMIAL OF LINE---

(-1.508E-03) + (7.660E-01)*X + (2.519E-01)*X^2
THE VARIANCE - 6.654E-05

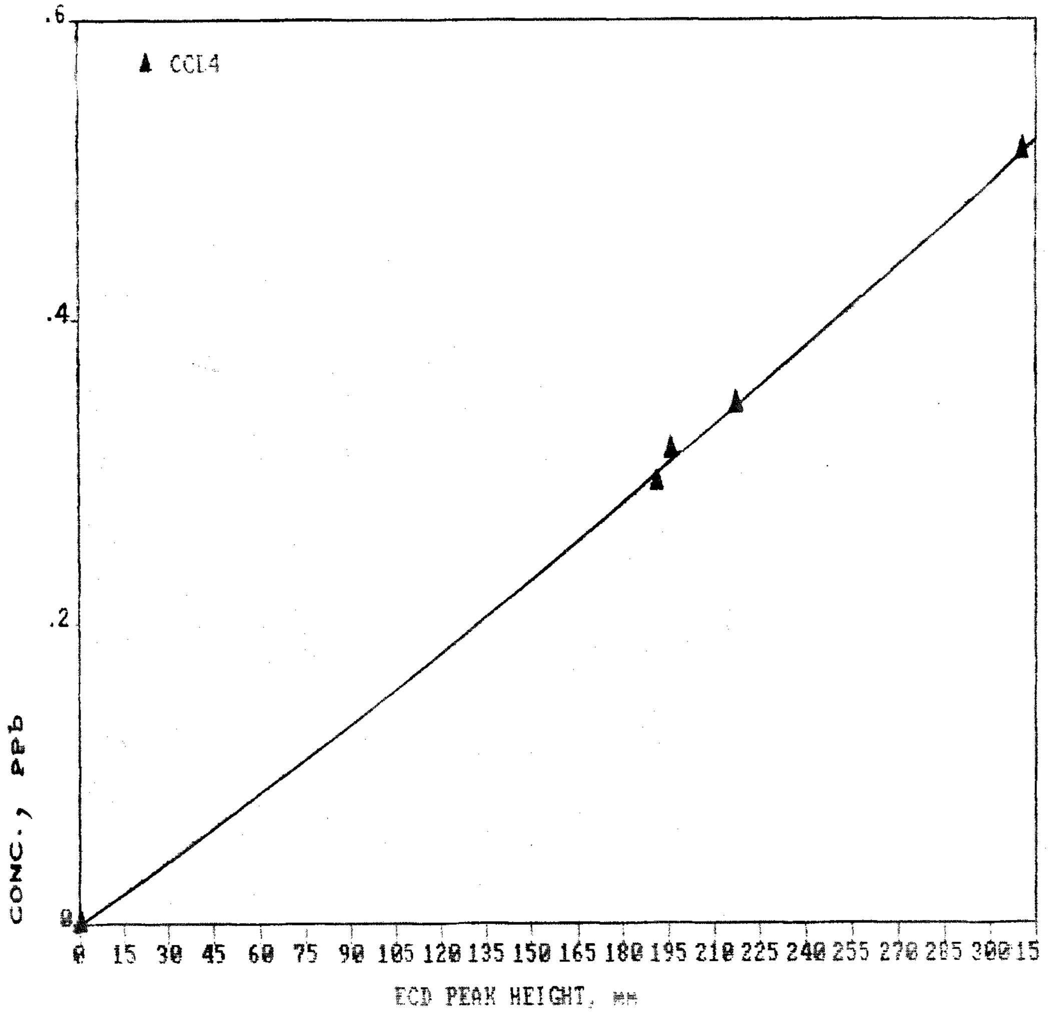
Figure 3.10 Calibration with ECD peak height fot 111*



THE REGRESSION POLYNOMIAL OF LINE---

$(7.929E-03) + (5.853E-01)*X + (1.668E-01)*X^2$
THE VARIANCE - 3.698E-05

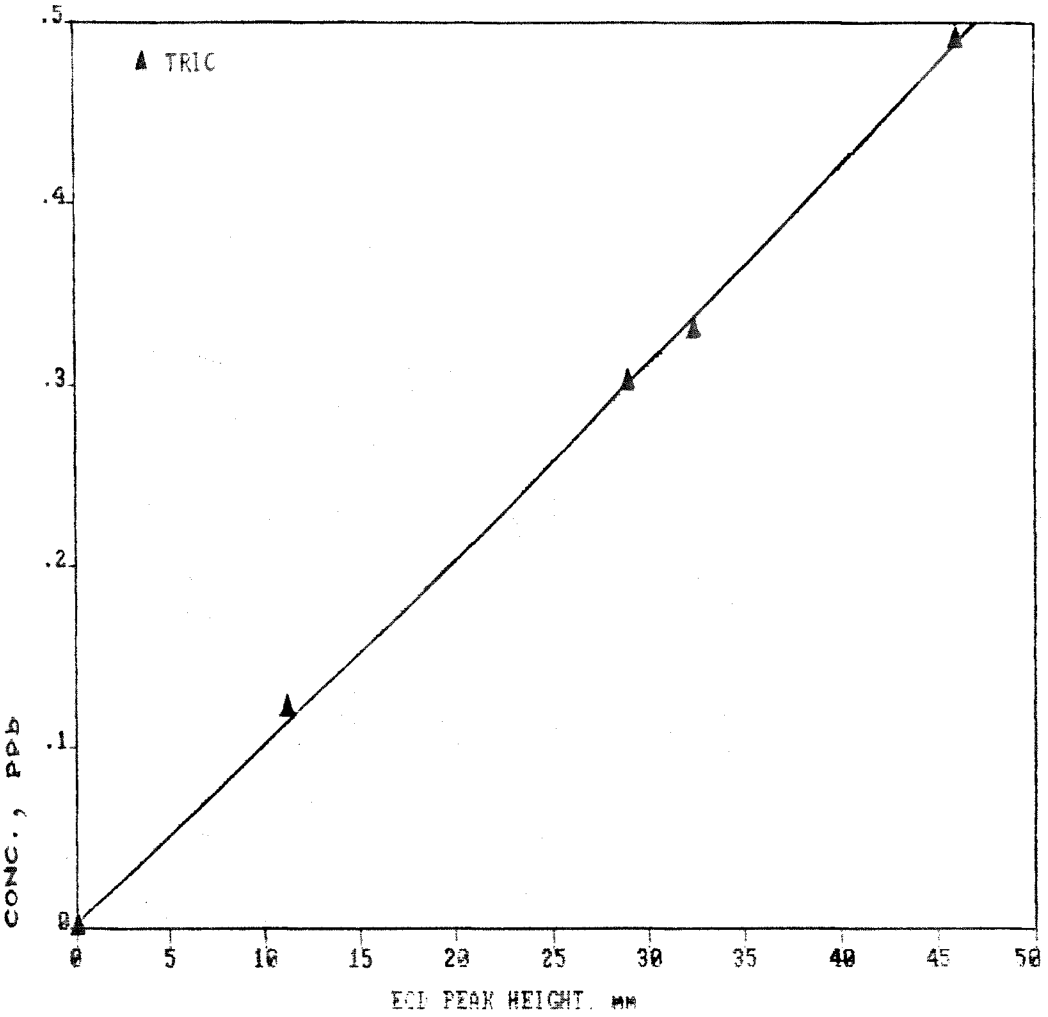
Figure 3.11 Calibration with ECD peak height fot CCL4



THE REGRESSION POLYNOMIAL OF LINE---

$(-5.162E-05) + (4.392E-01)*X + (7.857E-02)*X^2$
THE VARIANCE - 1.245E-05

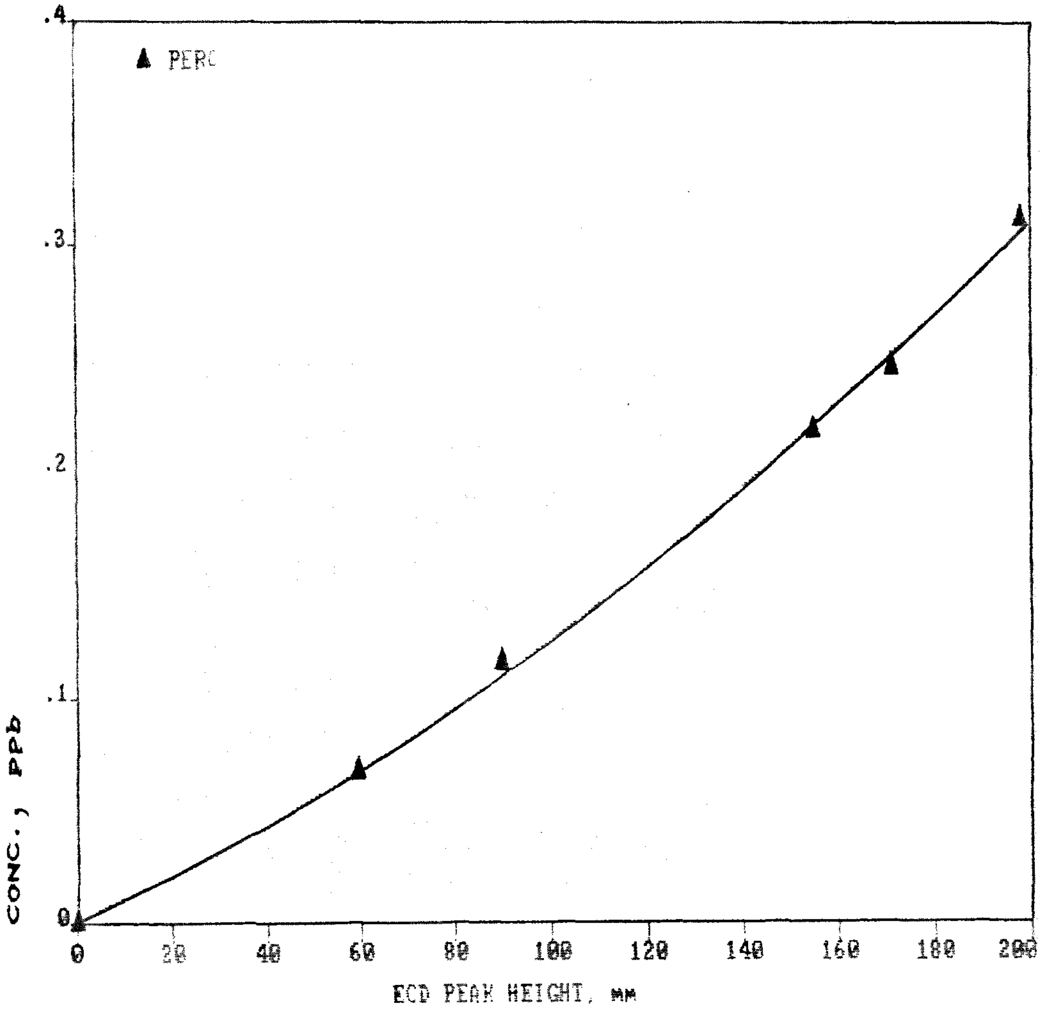
Figure 3.12 Calibration with ECD peak height fot TRIC



THE REGRESSION POLYNOMIAL OF LINE---

$(3.213E-03) + (4.820E-01)*X + (4.807E-02)*X^2$
THE VARIANCE - 2.122E-05

Figure 3.13 Calibration with ECD peak height for PERC



THE REGRESSION POLYNOMIAL OF LINE---

(1.133E-03) + (1.887E-01)*X + (1.181E-01)X^2
THE VARIANCE - 1.658E-05

4. COMPARISONS BETWEEN THE TENAX TRAP AND THE CANISTER COLLECTION METHODS.

A. Recovery efficiency

A series of experiments were conducted on the two systems respectively for determination of recovery efficiencies. For the Tenax trap system, the standard gas mixture was directed through traps up to a volume that is indicated by an accurate pressure gauge, for eight replicates. Then the traps were analyzed.

As for the Canister system, the standard gas mixture was filled into a Canister as a spiked sample and then was analyzed for eight replicates also. The recovery efficiencies were calculated and are compared as shown in Table 4.01.

Individual recovery rate of each compound varies from 20.83 % (MECL) to 120.87 % (PERC) in the Tenax trap system. While in the Canister system, it ranges from 68.18 % (MECL) to 120.95 % (DCM).

The average recovery rates are 98.35 % and 95.70 % in the Tenax trap and the Canister systems respectively. The sum of the percentage differences are -23.39 % and -53.85 % in the two systems.

Several findings are discussed as follows:

a. The recovery efficiency for MECL in the Tenax trap system is as low as 20.83 %

MECL has been known for its low retention volume (V_R); and low maximum sampling volume (MSV).

$$MSV \simeq 0.8\ V_R \quad [18]$$

A list of MSVs on Tenax-GC for some compounds is shown in Table 4.02 [18]. Moreover, purge-out experiments in the Air Pollution Research Laboratory confirmed the weak adsorptions of MECL and DCM on the Tenax.

In the Canister system, incomplete recovery (68.18 %) apparently results from an incomplete trapping in the cold bath at -110 °C. MECL can be quantitatively trapped at temperatures no higher than -160 °C as shown by preliminary experiments.

b. The recovery rates for the heaviest two compounds; PMX and OX, in the Canister system are below 90 %, possibly because the transfer line in the system is heated to 60--80 °C, which is not hot enough to maintain these two compounds in vapor phase during the transfer. In other words, PMX and OX are partially lost in the transfer line through condensing. This is confirmed by the experiments on temperature effect of transfer line, results of which are shown in Figure 4.01 and 4.02 [13].

c. On the contrary, PERC, PMX and OX in the Tenax trap systems appeared in recovery percentages higher than 100. The likely reasons are either incomplete desorption during trap cleaning process, which causes carryover, or diffusion of these strongly adsorbed compounds onto the Tenax from the ambient air during storage of the blank traps, or both.

Certain problems and related discussions associated with storage of blank traps are to be mentioned in 4.E.b.

B. Reproducibility

The same experiments also evaluated the reproducibility of the two systems. The results are listed in Table 4.03. The coefficients of variation (C.V. %) of the 11 target compounds other than MECL are all within 15 %. If MECL is omitted, since it has been shown to have intractable difficulties in both systems, then the average C.V.% will be 6.00 % in the Tenax trap system and 6.24 % in the Canister system.

Therefore, the systems themselves show fairly good reproducibilities.

C. Concentrations of individual target compounds

Analytical results that are used for comparisons are of air samples collected from 10/24/88 till 2/09/89, and from the Carteret and the Elizabeth sites. A total of 15 and 17 air samples were available from the two sites.

Figures 4.03 through 4.13 show the plots of concentrations of the target VOCs. It can be seen that for C6, 111*, BZ, TRIC, TOL, PERC, PMX, and OX, Figures 4.03 to 4.10 correspondingly, the two plots of Canister and Tenax data for the Carteret site show similar levels and trends. This fact is confirmed by the counterpart plots for the samples from the Elizabeth site. (Figures 4.11 to 4.18 correspondingly).

However, for MECL, CFOR, and CCL4, the plots show less agreement between the two systems as seen in Fugures 4.19 to 4.21 for the Carteret site and 4.22 to 4.24 for the Elizabeth site, respectively. For each of these compounds various and likely reasons are associated with the weaknesses of either the Tenax trap system or the Canister system, or both, which are as follows:

a. MECL can not be trapped completely either on Tenax GC or in the cryogenic trap (at -110 °C) of the Canister system as related in 4.A.a.

b. DCM also shows comparatively low retention volume in the purge-out experiments [13]. However, the experiments for recovery efficiencies yielded the recovery rate of DCM no less than 100 %. There are likely two reasons:

   i. The flow rate for the recovery experiments was lower than that for the purge-out experiments, appromately 1.5 ml/min. and 4.8 ml/min. respectively. That indicates that sampling rate has certain effects on adsorption efficiency of an adsorption medium as well as sampling volume does.

ii. The adsorption of DCM on Tenax-GC is probably interferred with the presence of water vapor and/or of other VOCs in the ambient air samples.

c. The electron capture detector (ECD) in the Tenax trap system is not sensitive enough to chloroform for the the system has yielded result of zero for a long period, thus no comparison with the Canister data can be made. The reason of the insensitivity is unascertained.

d. CCL4 does not appear to be efficiently trapped by the Tenax, most likely because of the low polarity of its molecular structure. In addition, there is some evidence that reveals losses of the compound as it is stored in the stainless steel Tenax trap after sampling, and as it passes through the stainless steel tubing during analysis [19]. These can account for the lower concentration level from the Tenax trap system than that from the Canister system.

D. General property

Other than those characteristic discussed above, some comparisons in general properties, though they may seem minor, are submitted as follows:

a. Ease of operation

It is doubtless that the Tenax trap method is easier and more convenient in operation, as microprocessor controlled automatic thermo-desorption apparatus are commercially available. For the Canister collection method, most of the operations are carried out manually by use of home-made devices, because parts of the procedures were tentative, until the results were acknowledged as successful and were recognized by the EPA. Examples are; the use of SUMMA polished Canisters, the glass-bead-filled preconcentration trap, and the trial of -110 ^{o}C cold trap of n-propanol slush instead of -180 ^{o}C liquid argon, etc.

b. Sample-loss rate

On the other hand, the Canister collection method possesses the advantage of prevention of lost samples.
An estimate of sample-loss rate indicates that the frequency in the Tenax trap system is 3.5 times of that in the Canister system, if one pair of the traps (high and low flow rates) can be regarded as a complete air sample only.

The losses of samples occurred inevitably and most often by reasons of malfunction of the instruments, computer A/D conversion, slips in the operation, or any problems in the Tenax packing bed , such as conglomeration, plugging, channelling, or deterioration, of Tenax-GC polymer. As the analyte is irretrievable, and every

Tenax trap sample is unique, any unforeseen troubles will render a poor sample or a lost one. Whereas for the Canister analysis, a Canister at even merely 5 psig would be sufficient for 5--6 analyses. Normally the Canister samples are at around 14 psig, containing plenty of air for repeat analyses, when interruption or abortion of an analysis is caused by the incidences foresaid.

E. The deficiencies of the Tenax trap method

After the study, the deficiencies of the Tenax trap method are defined as follows:

a. The break-through issue

This issue has been a major concern in studies and developments of the use of Tenax-GC. The polymer has been satisfactorily applied in adsorption of C_2--C_{16} VOCs. However, as collection efficiency is influenced by many parameters, such as sampling flow rate, maximum sampling volumes of each interest VOC, temperature, and humidity of the atmospheric air, etc., breakthrough of some of the components is somewhat inevitable, especially when one attempts to use the Tenax for a wide range of VOCs or when the application covers light hydrocarbons or low molecular weight polar compounds [13].

Figures 4.25 to 4.27 present the deviations between concentrations in traps of high and low flow rates, for

MECL, 111*, and BZ from the Carteret site, which show considerable disagreements between the two traps.

It should be noted that the analoges for samples from the Elizabeth site, Figures 4.28 to 4.30 show deviations between the two traps typically less extent than that from the Carteret site. This contrast may suggest an interference existing among the components of the air samples, which affects the breakthrough volume, as it has been found that the constitutions of the air samples from the two sites are quite different.

b. The background contribution

Blank traps are carried to the sites and are analyzed along with the other two traps in accordance to the project requirements. This study observed that typically five compounds of interest have been detected in every blank trap. They are MECL, BZ, TOL, PMX, and OX.

The comparison for concentrations of these compounds in blank traps and the average concentrations of the two traps is listed in Table 4.05. MECL posses the most background contribution, then BZ. The overall averages of the percentages of blank traps over two-tube averages are as follows:

72.71 , 11.49 , 4.02 , 1.66, & 1.33 % for :
MECL, BZ, OX, PMX ,and OX, correspondingly.

The origin of the background is not ascertained. Desorption efficiency of the Tekmar desorber was checked by analyzing a sampled trap immediately after it had been desorbed, and the trap was proved free of any background. Most probably, diffusion of these compounds from the laboratory air during storage can account for the background. Normally, blank traps are stored at room temperature for 4 or 5 days before next sampling. For the extremely high percentage of blank trap over average of two tubes for MECL , the possible reason is ; the blank is undesirably high due to diffusion from the ambient air into the trap, while the sampled traps are unexpectedly low due to diffusion also occurring out from the traps, plus the known breakthrough problem. It has been felt that MECL concentrations consistently show at a level lower than should be, because many hydrocarbons easily form MECL in the presence of chloride and sunlight.

c. The necessity for temperature correction

Since concentrations of air sample components involve the total sample volume according to Equation (4) in 2.B.d, and the latter varies with temperature as indicated by the formula: $P_1 V_1 / T_1 = P_2 V_2 / T_2$, and the outdoor temperature in the coldest season could be as low as -10 ^oC, while 38 ^oC in the hottest weather, it becomes indispensible to make temperature corrections to the analytical results. Currently the correction factors adopted by the EPA/NJDEP are ; 1.10 for months of November to February, 1.07 for March to May, and 1.03 for June to October, and are calculated by using the average highest temperature in the season normalized to room temperature 25 ^{o}C. This approach appears too rough to accurately rectify the results and improve their overall reliability, since the the atmospheric temperature varies much even in a season. Nevertheless, it is considered a convenient implementation of temperature correction for the results from the Tenax trap method. Otherwise, it would become tedious and troublesome if one attempted to make the correction by taking account of daily outdoor temperatures.

Thus, the best method for temperature correction is still an open issue.

F. The deficiencies of the Canister collection method

a. The difficulties in automation

It has been a long term attempt to automate the procedures of the Canister system by connection to the Tekmar desorber assembly. However, some difficulties resulted in failures, such as water plugging in the precolumn of the GC column, and determination of an optimum transfer line temperature, and so on. Certain considerable breakthrough and solutions of the problems have been achieved up to the present time in the Air Pollution Research Lab.

b. Water plugging in the preconcentration trap

Occasionally frost, which is frozen from water vapor in the air sample, aggregates in the preconcentration trap of 1/16 inch id stainless steel tube packed with glass beads. The conglomerates, though they may be tiny, are comparatively large enough to block the channels among the glass beads and those between the beads and the tube wall. This stops either the sample loading flow or later hinders the transfer of re-vaporized VOCs.

This is prone to occur more frequently in summer or when a series of analyses have been continuously done. This finding may suggest that the conglomerates are formed of a mixture of frost from water vapor and accumulated residues, which is in a frozen form, from the preceding analyses. The problem is solved simply by heating the preconcentration trap exteriorly.

Table 4.01 Recovery efficiencies of the two systems

		Tenax trap			Canister		
	Compounds	AVG. RCV %	DIF. %	C.V. %	AVG. RCV %	DIF. %	C.V. %
1	MECL	20.83	-79.17	28.99	68.18	-31.82	35.17
2	DCM	103.66	3.66	6.64	120.95	20.95	3.87
3	C6	99.58	-0.42	2.42	95.74	-4.26	5.04
4	CFOR	99.01	-0.99	7.56	108.60	8.60	3.03
5	111*	97.73	-2.27	4.80	92.50	-7.50	13.70
6	BZ	108.15	8.15	3.09	100.00	0.00	3.52
7	CCL4	103.63	3.63	9.81	100.85	0.85	12.47
8	TRIC	96.30	-3.70	7.61	95.45	-4.55	3.21
9	TOL	105.40	5.40	4.08	93.39	-6.61	3.16
10	PERC	120.87	20.87	6.11	97.45	-2.55	4.32
11	PMX	112.38	12.38	11.81	83.33	-16.67	11.14
12	OX	112.70	12.70	8.10	89.71	-10.29	10.77
	Average Recovery %			98.35		95.51	
	Sum of % Difference			-20.76		-53.85	

Table 4.02 Maximum sampling volumes of some VOCs,
in liter of air/gm of Tenax-GC

	at 20 °C	38 °C (estimated)
MECL	0.12	
DCM	0.52	
CFOR	2.04	8
111*	5.77	6
BZ		19
CCL4	3.46	8
TRIC	8.85	20
TOL		97
PMX & OX		200

Table 4.03 Reproducibilities of the two systems

Compounds	Tenax trap AVG. ng	Tenax trap SD ng	Tenax trap RSD %	Canister AVG. ng	Canister SD ng	Canister RSD %
1 MECL	1.85	0.54	28.99	2.25	1.16	35.17
2 DCM	60.94	4.05	6.64	26.85	0.86	3.87
3 C6	38.11	0.92	2.42	13.50	0.71	5.04
4 CFOR	88.40	6.68	7.56	36.00	1.00	3.03
5 111*	51.60	2.48	4.80	22.20	3.29	13.70
6 BZ	47.35	1.46	3.09	16.20	0.57	3.52
7 CCL4	96.84	9.50	9.81	35.70	4.41	12.47
8 TRIC	68.32	5.20	7.61	25.20	0.85	3.21
9 TOL	62.31	2.54	4.08	16.95	0.57	3.16
10 PERC	76.75	4.69	6.11	22.95	1.02	4.32
11 PMX	24.71	2.92	11.81	6.75	0.90	11.14
12 OX	31.49	2.55	8.10	9.15	1.10	10.77
Average Relative Standard Deviation			8.42 %		9.17 %	

Table 4.04 Comparison of concentrations of blank trap and average of two-tubes, Carteret site.

	MCEL		BZ		TOL		PMX		OX	
	Blnk	Avg	Blnk	Avg	Blnk	Avg	Blnk	Avg	Blnk	Avg
10/06/88	0.20	0.19	0.24	1.66	0.05	5.45	0.07	1.77	0.02	0.56
10/12	0.13	0.38	0.13	0.75	0.03	1.93	0.01	0.77	0.00	0.27
10/18	0.16	0.32	0.22	1.90	0.03	3.00	0.00	2.08	0.00	0.96
10/24	0.18	0.26	0.14	1.44	0.04	6.78	0.01	2.87	0.01	0.96
10/30	0.21	0.24	0.15	2.15	0.05	5.01	0.03	1.65	0.00	0.54
11/05	0.15	0.13	0.10	0.37	0.04	0.88	0.02	0.29	0.07	0.12
11/11	0.30	0.12	0.22	1.61	0.13	4.07	0.01	1.78	0.00	0.57
11/17	0.07	0.25	0.19	1.38	0.04	3.65	0.03	1.42	0.00	0.51
11/23	0.18	0.34	0.14	2.36	0.03	6.06	0.02	2 28	0.01	0.73
11/29	0.08	0.16	0.18	2.50	0.04	6.71	0.01	2.35	0.00	0.75
12/05	0.07	0.24	0.17	2.20	0.03	6.18	0.01	2.13	0.00	0.68
12/11	0.08	0.11	0.13	1.17	0.02	2.09	0.01	0.71	0.00	0.23
12/17	0.20	0.14	0.15	1.64	0.04	3.31	0.02	1.20	0.00	0.41
12/23	0.14	0.56	0.16	2.31	0.03	4.79	0.01	1.60	0.00	0.60
12/29	0.23	0.45	0.35	1.65	0.09	2.99	0.04	0.96	0.00	0.32

	MECL % Blk/Avg	BZ % Blk/Avg	TOL % Blk/AVG	PMX % Blk/Avg	OX % Blk/AVG
	105.26	14.46	0.92	3.95	3.57
	34.21	17.33	1.55	1.30	0.00
	50.00	11.58	1.00	0.00	0.00
	69.23	9.72	0.59	0.35	1.04
	87.50	6.98	1.00	1.82	0.00
	115.38	27.03	4.55	6.90	58.33
	250.00	13.66	3.19	0.56	0.00
	28.00	13.77	1.10	2.11	0.00
	52.94	5.93	0.50	0.88	1.37
	50.00	7.20	0.60	0.43	0.00
	29.17	7.73	0.49	0.47	0.00
	72.73	11.11	0.96	1.41	0.00
	142.86	9.15	1.21	1.67	0.00
	25.00	6.93	0.63	0.63	0.00
	51.11	21.21	3.01	4.17	0.00
Avg %	72.71	11.49	1.33	1.66	4.02

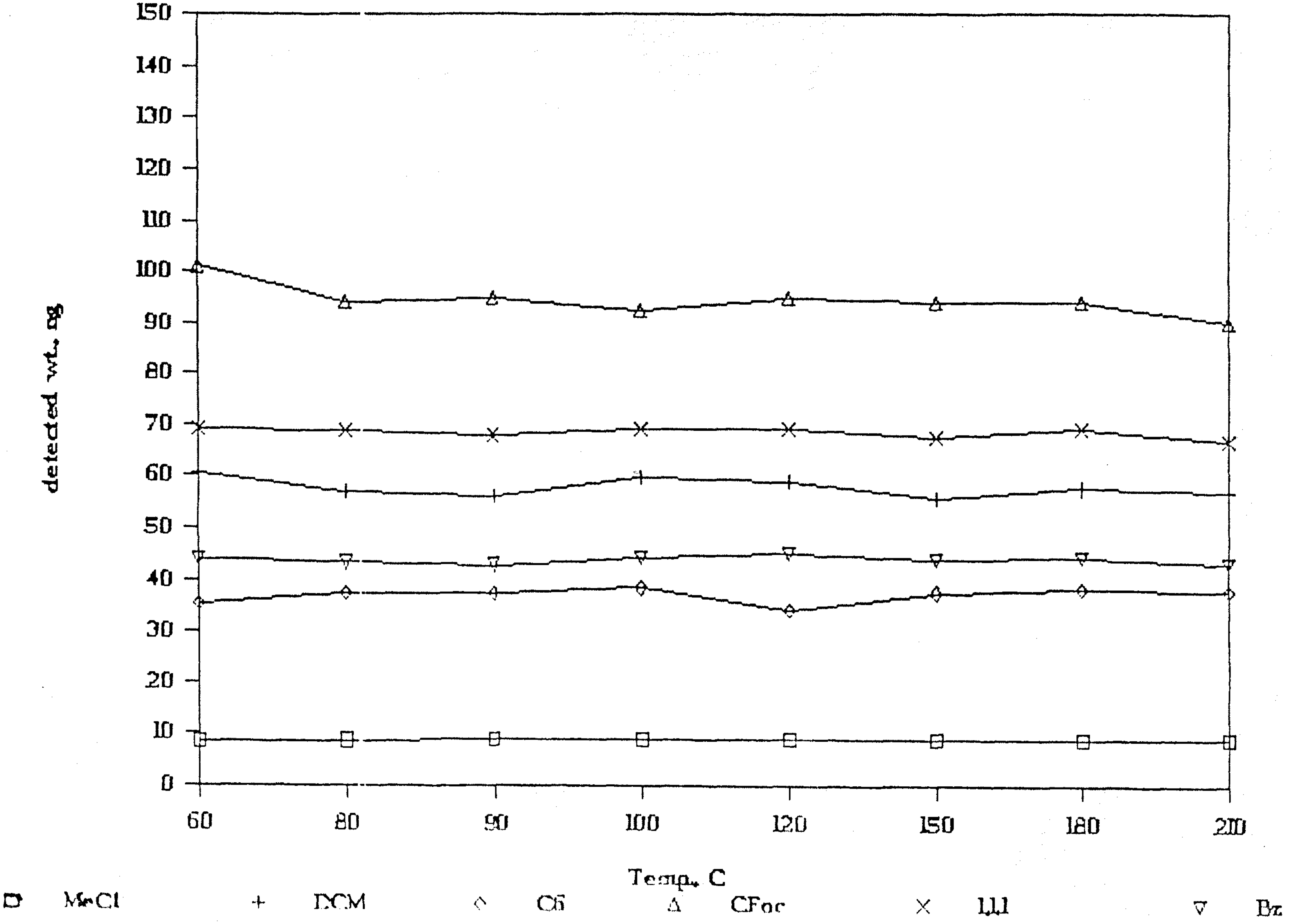


Figure 4.01 Temperature effect on transfer line
Low b.p. compounds

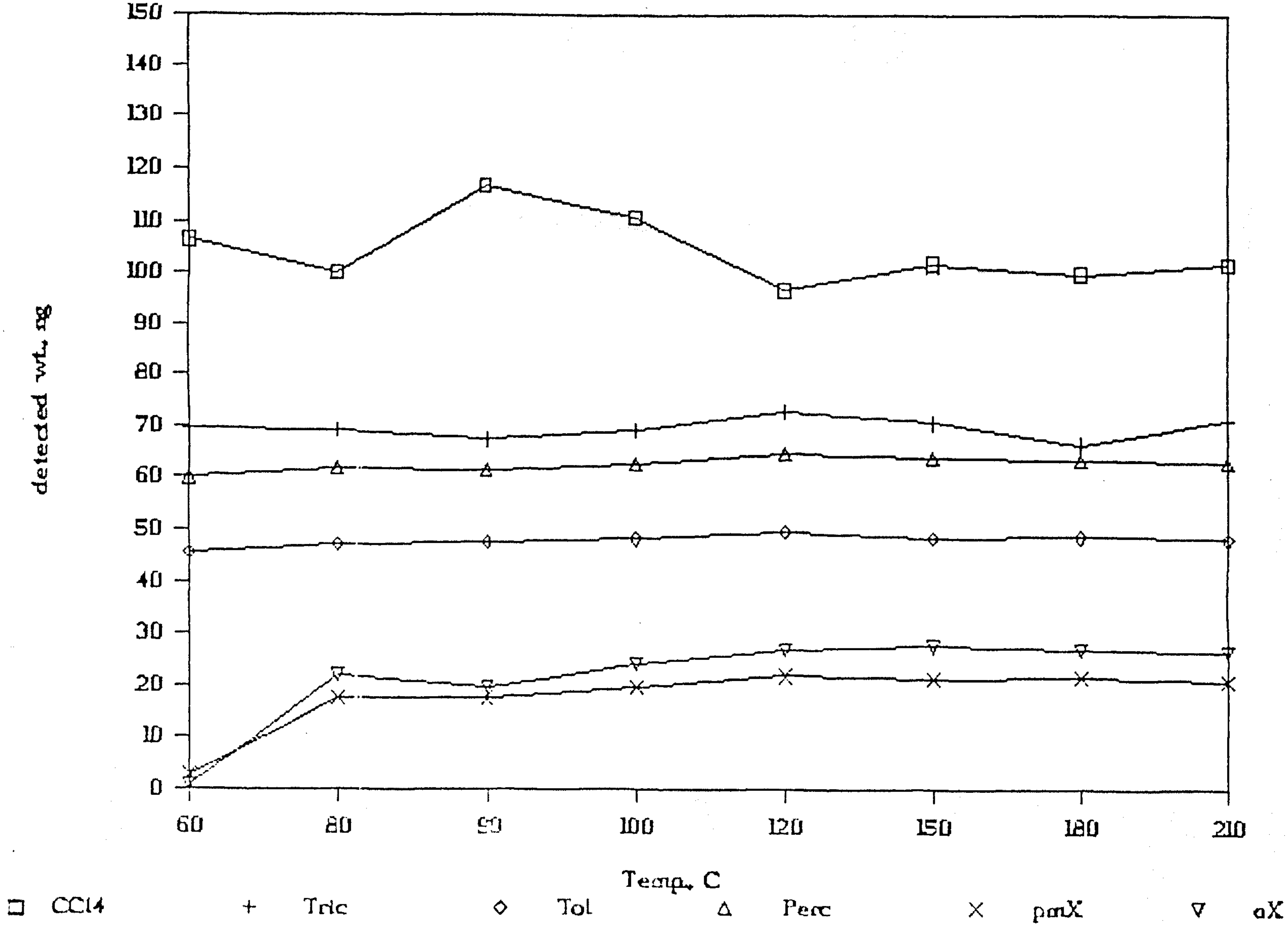


Figure 4.02 Temperature effect on transfer line
High b.p. compounds

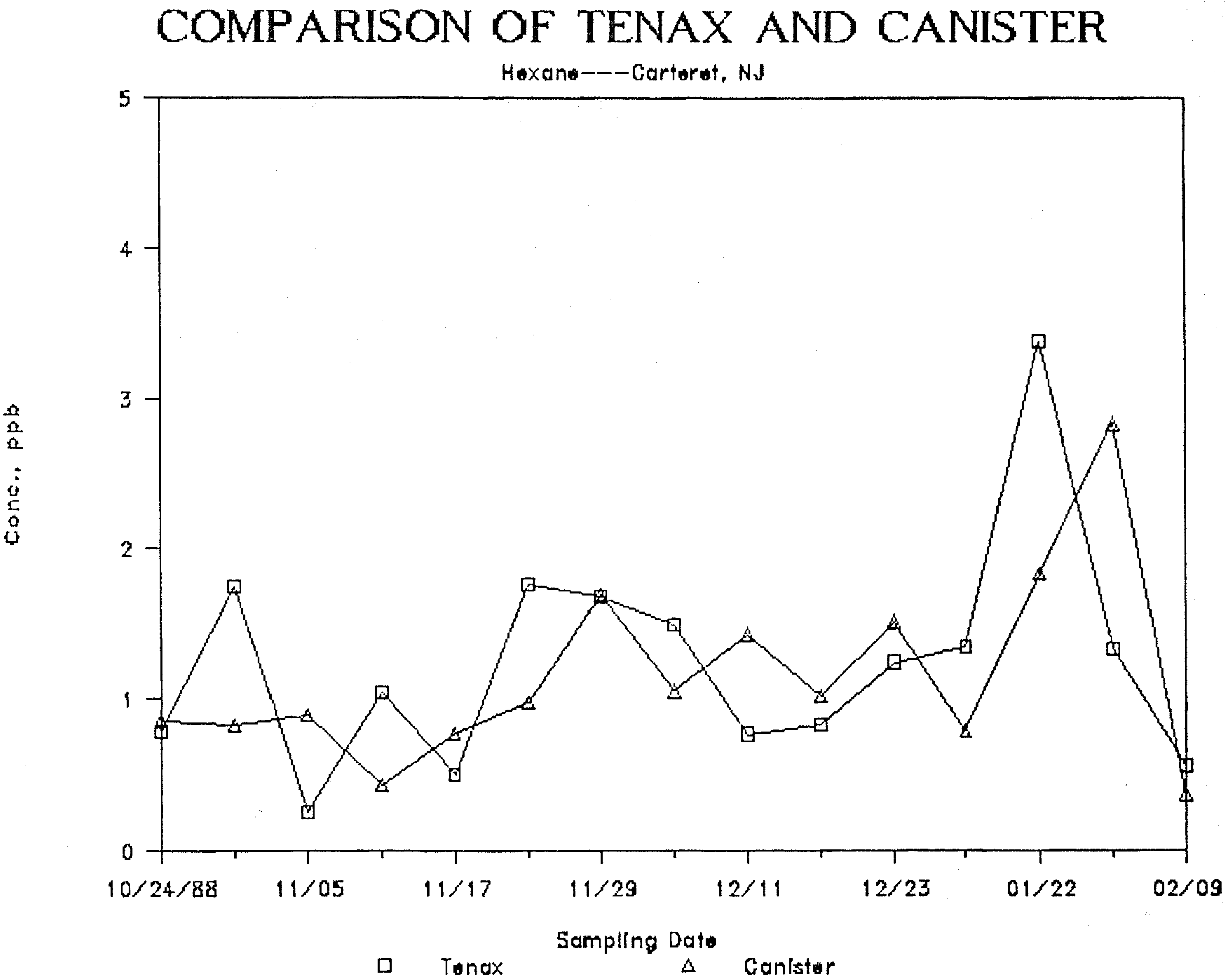


Figure 4.03 Concentration plots of C6, Carteret site

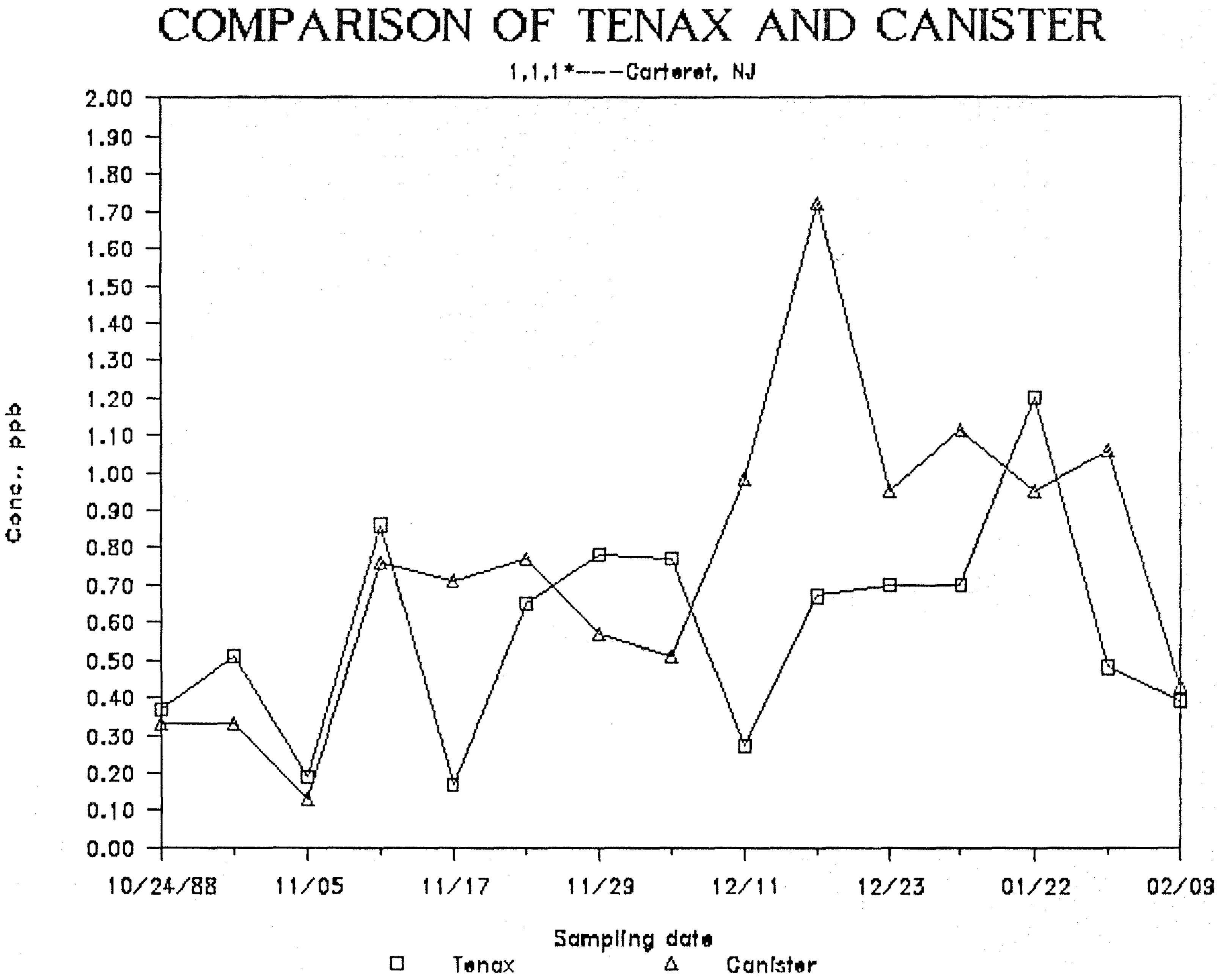


Figure 4.04 Concentration plots of 111* , Carteret site

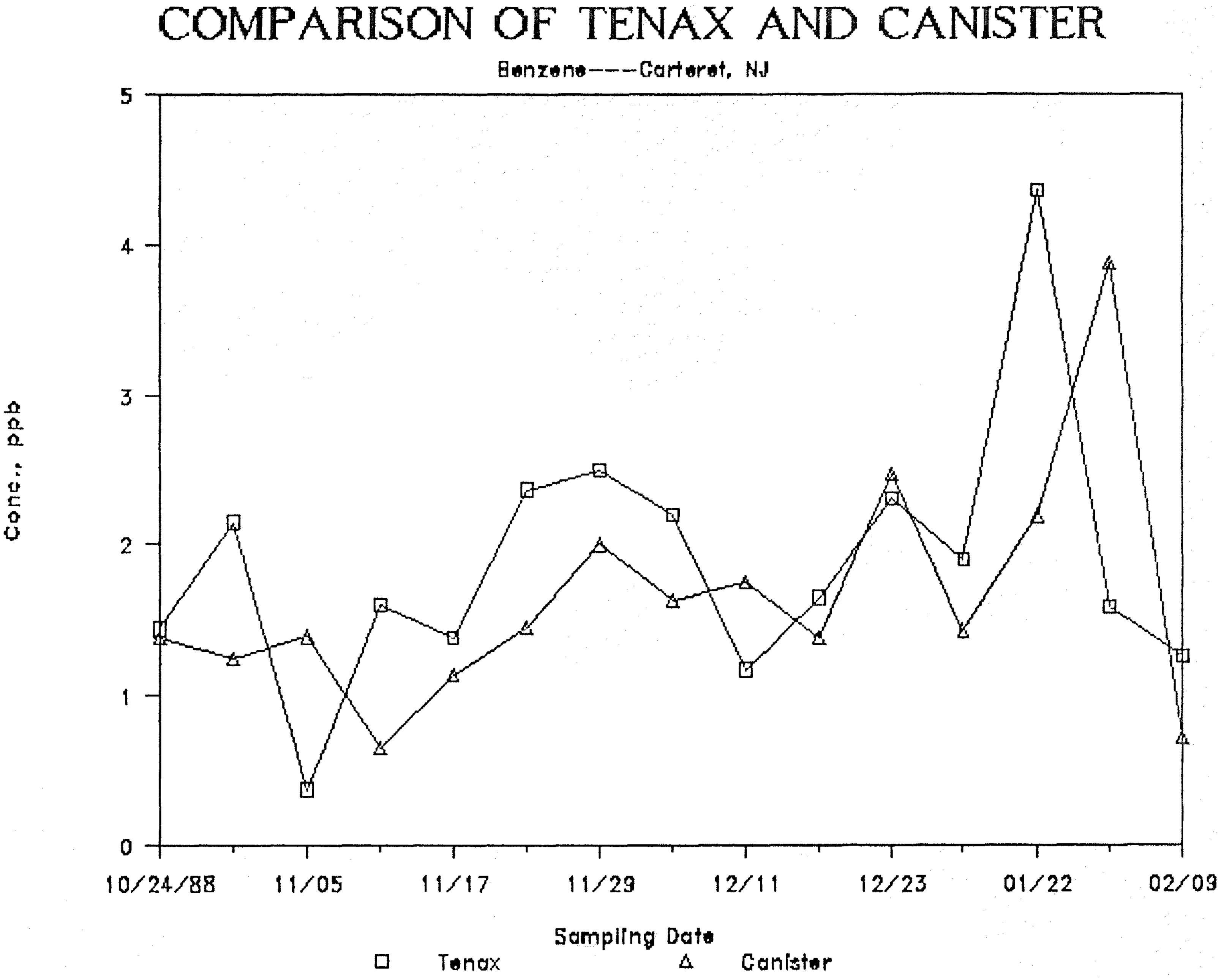


Figure 4.05 Concentration plots of BZ, Carteret site

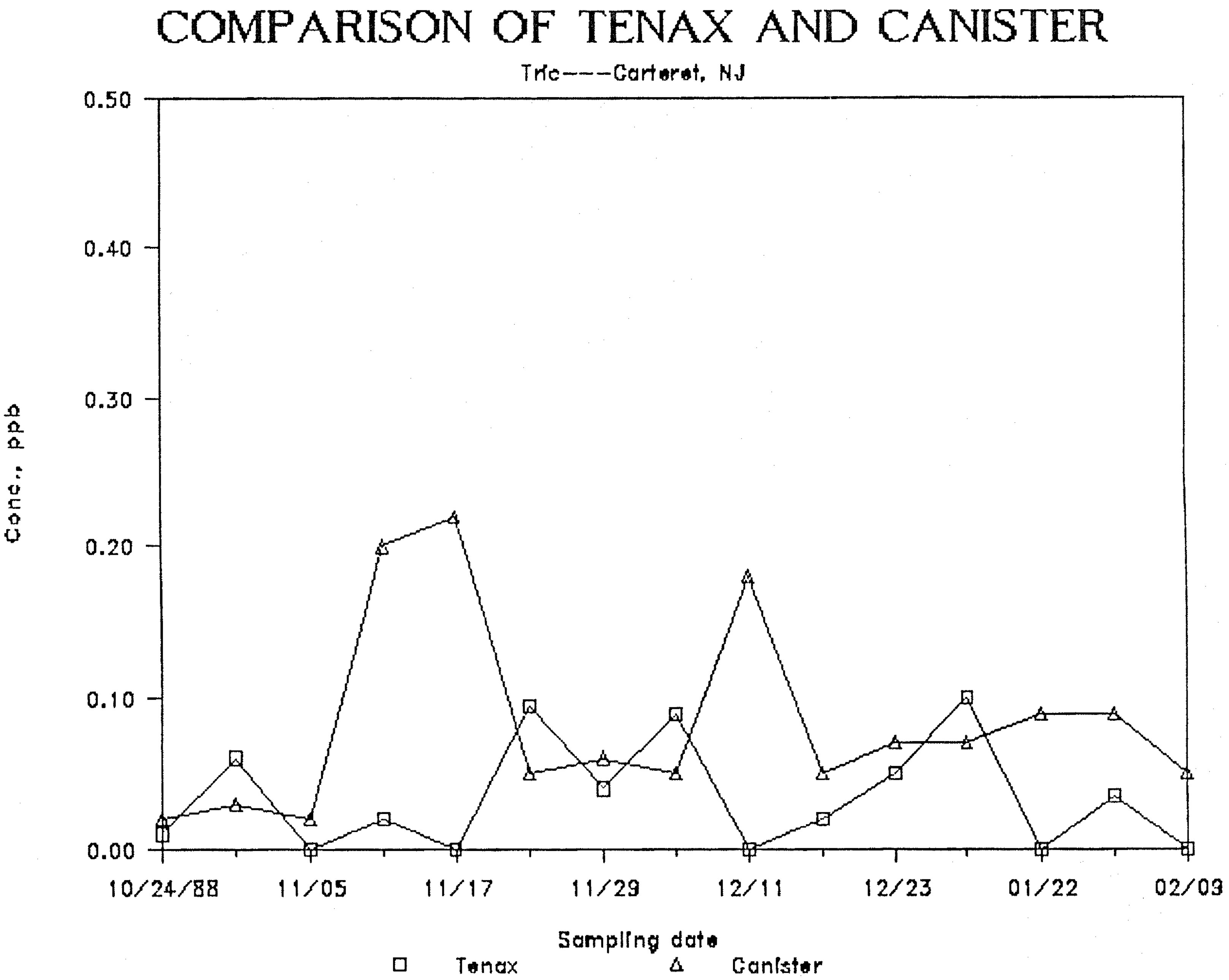


Figure 4.06 Concentration plots of TRIC, Carteret site

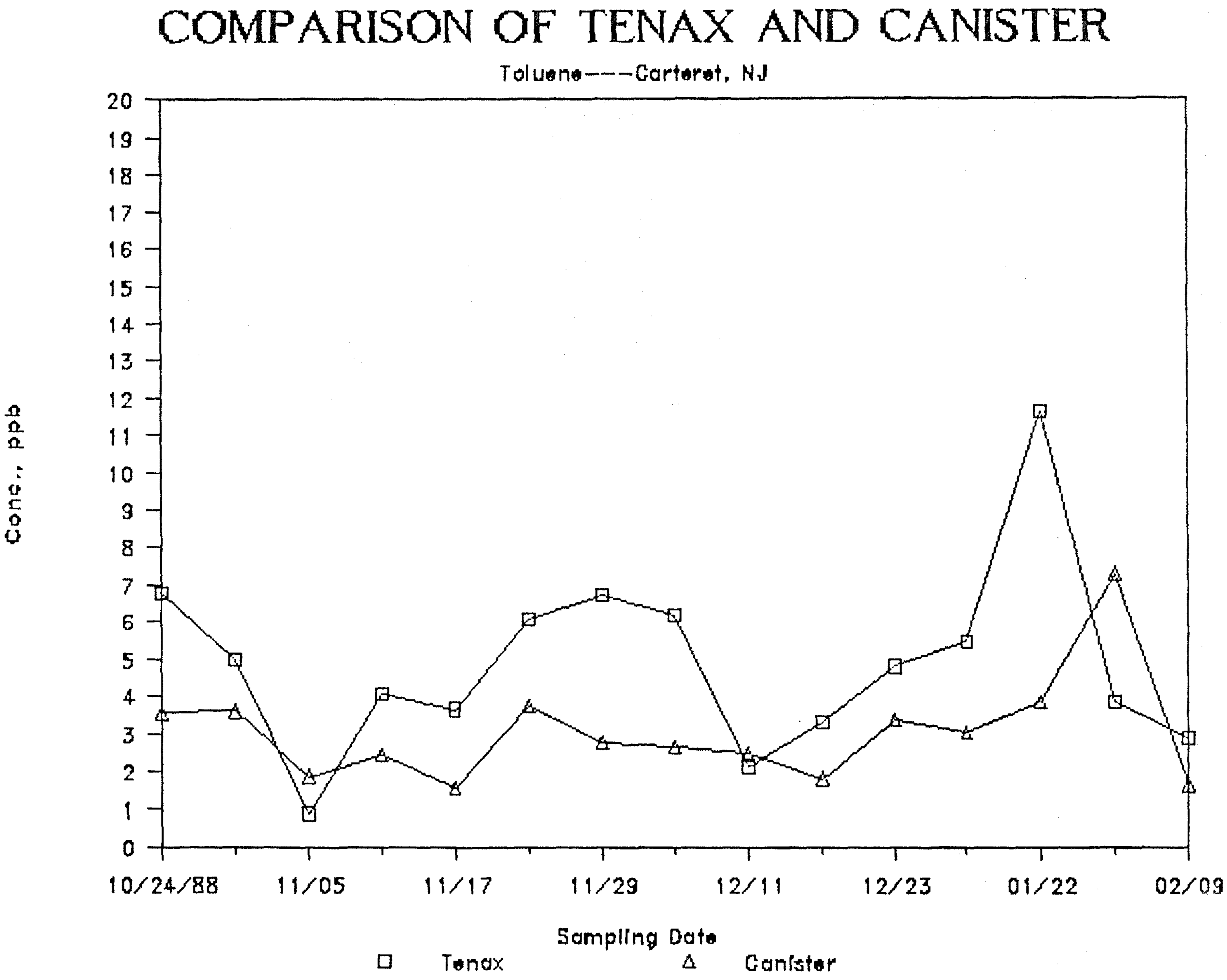


Figure 4.07 Concentration plots of TOL, Carteret site

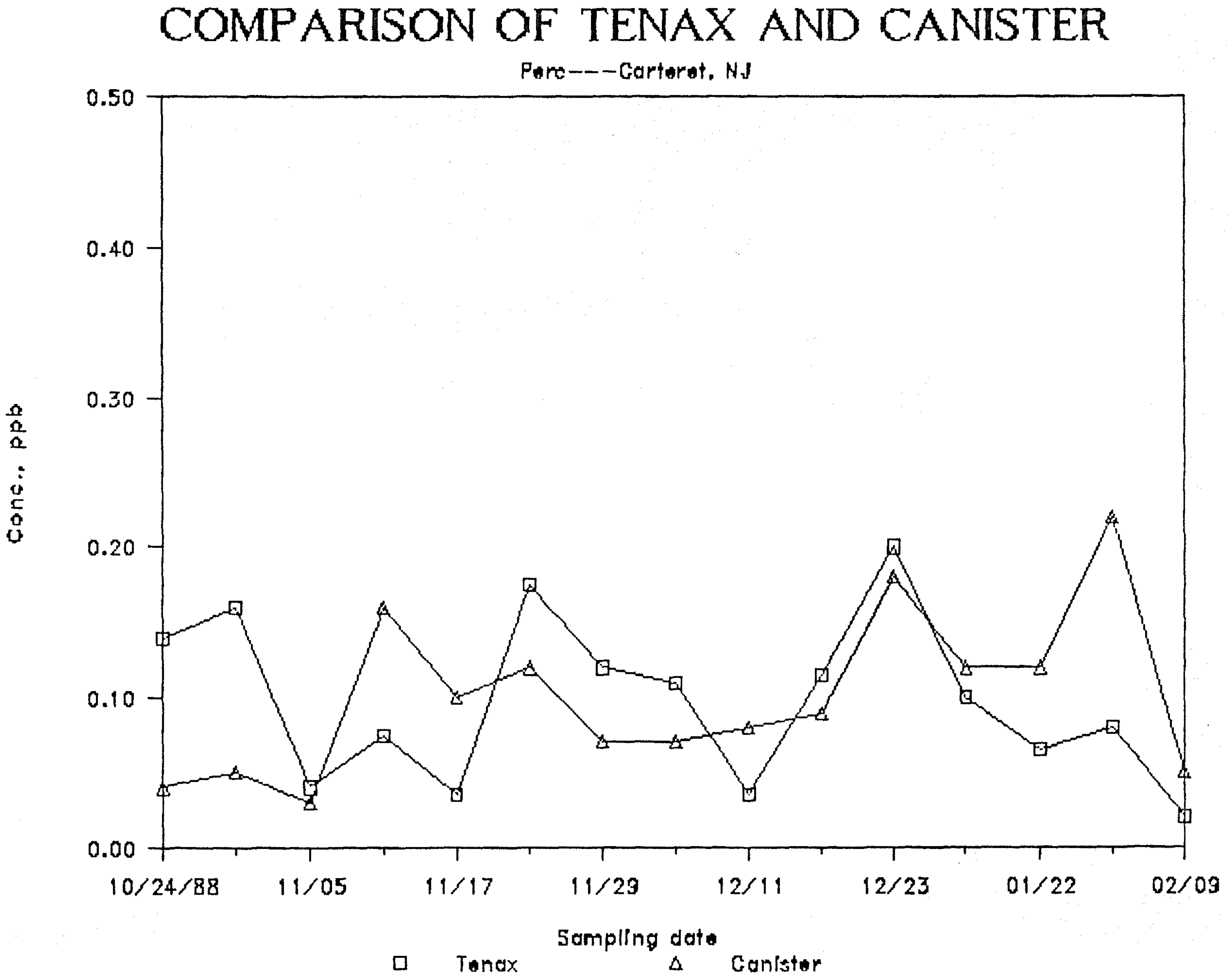


Figure 4.08 Concentration plots of PERC, Carteret site

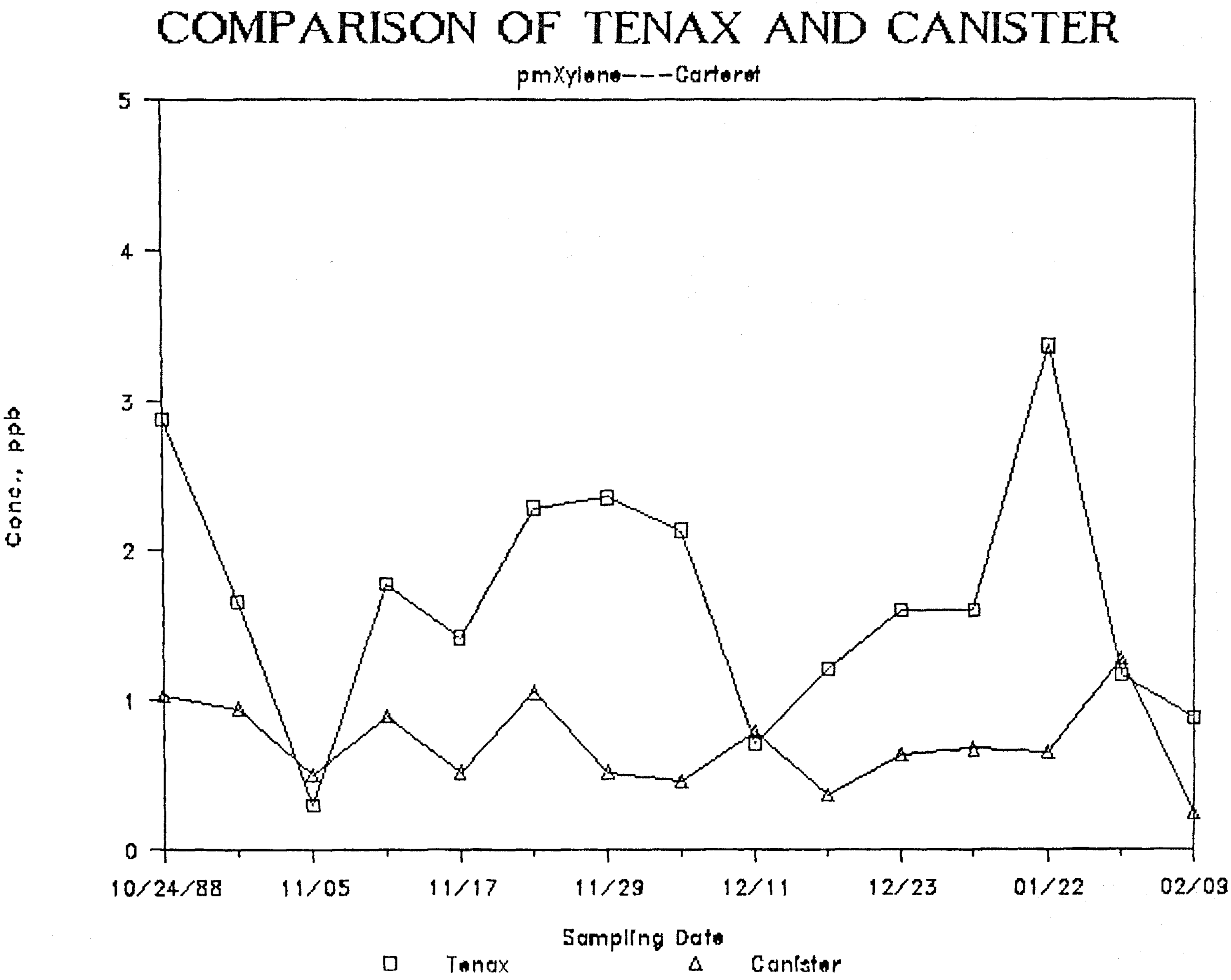


Figure 4.09 Concentration plots of PMX, Carteret site

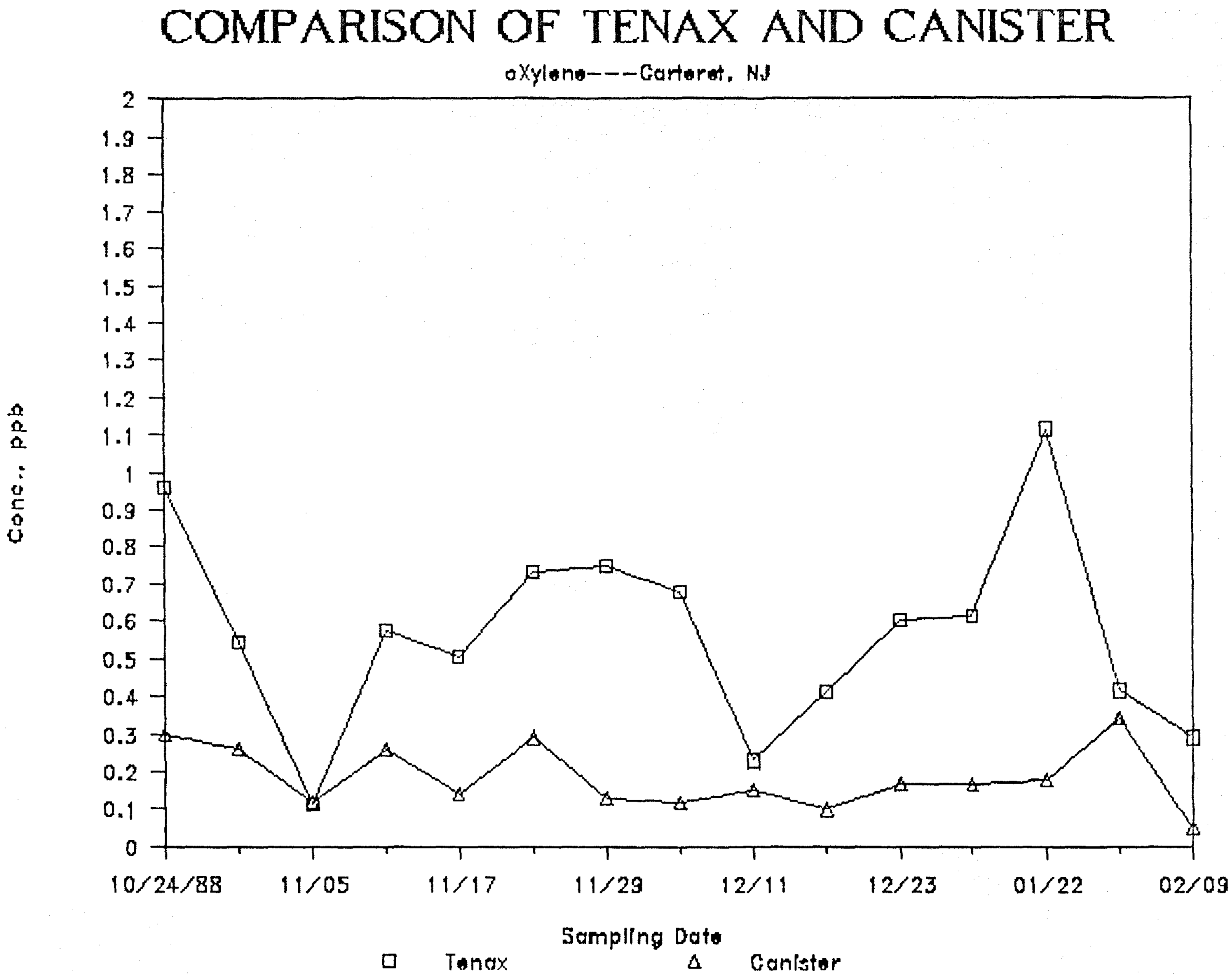


Figure 4.10 Concentration plots of OX, Carteret site

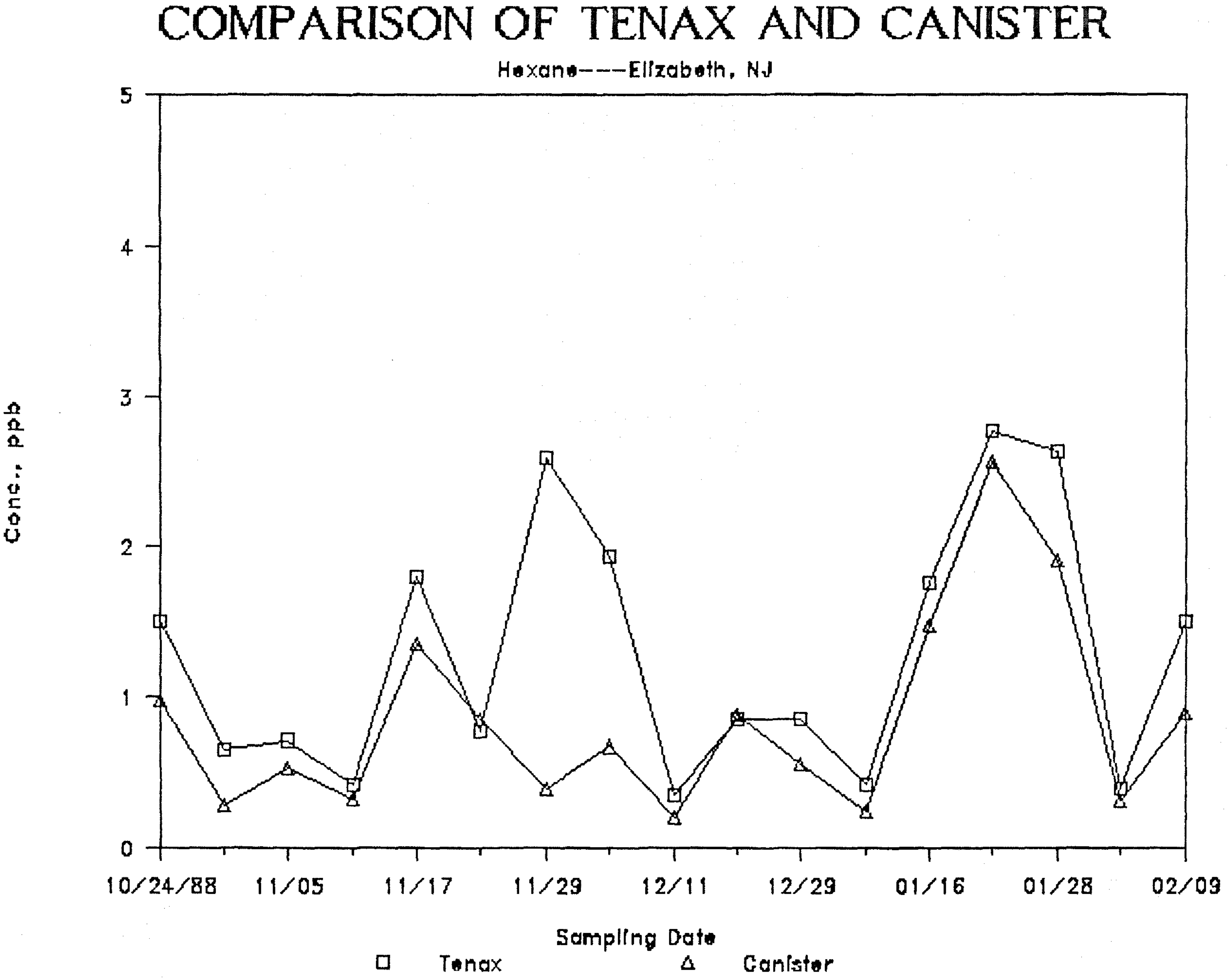


Figure 4.11 Concentration plots of C6, Elizabeth site

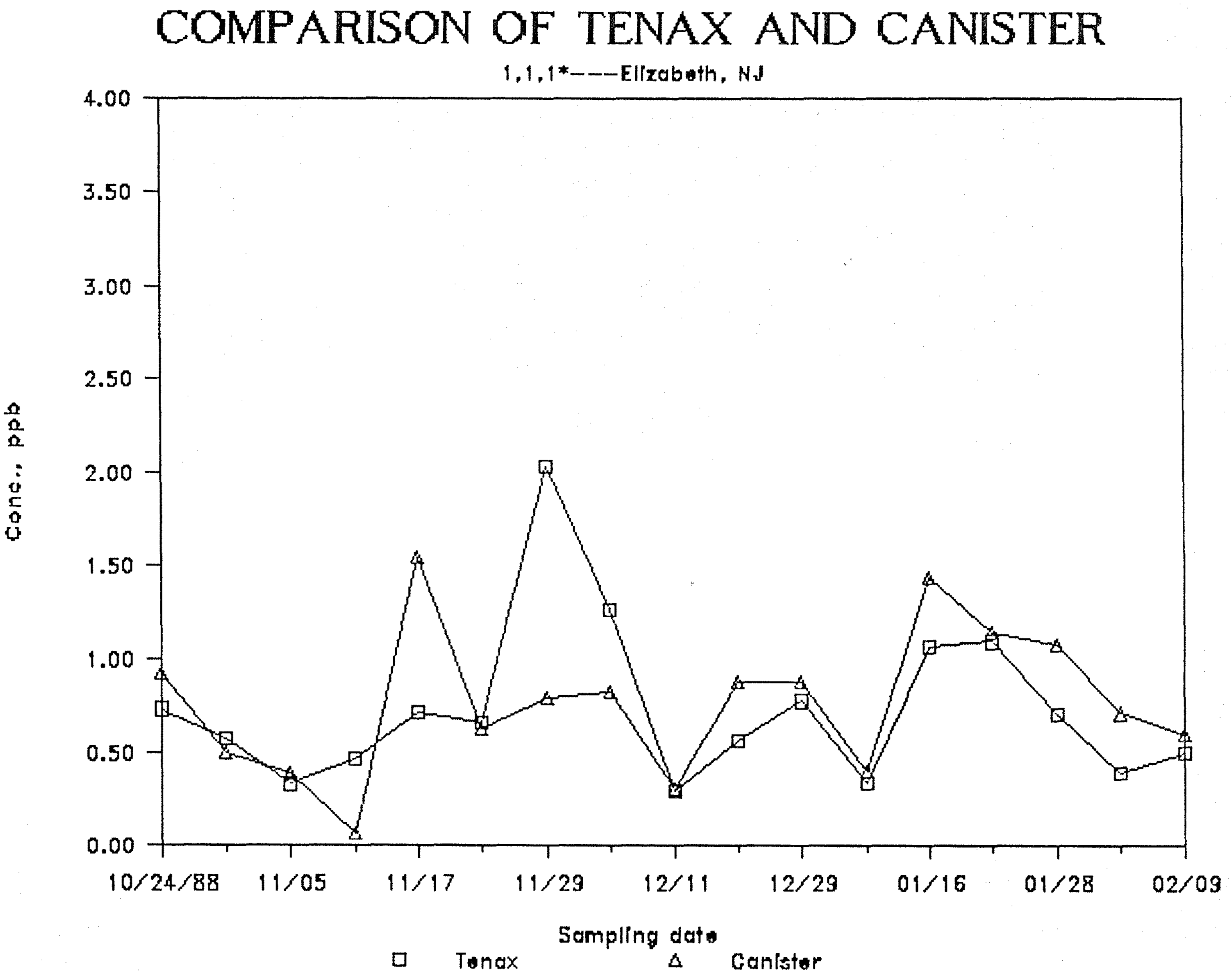


Figure 4.12 Concentration plots of 111* , Elizabeth site

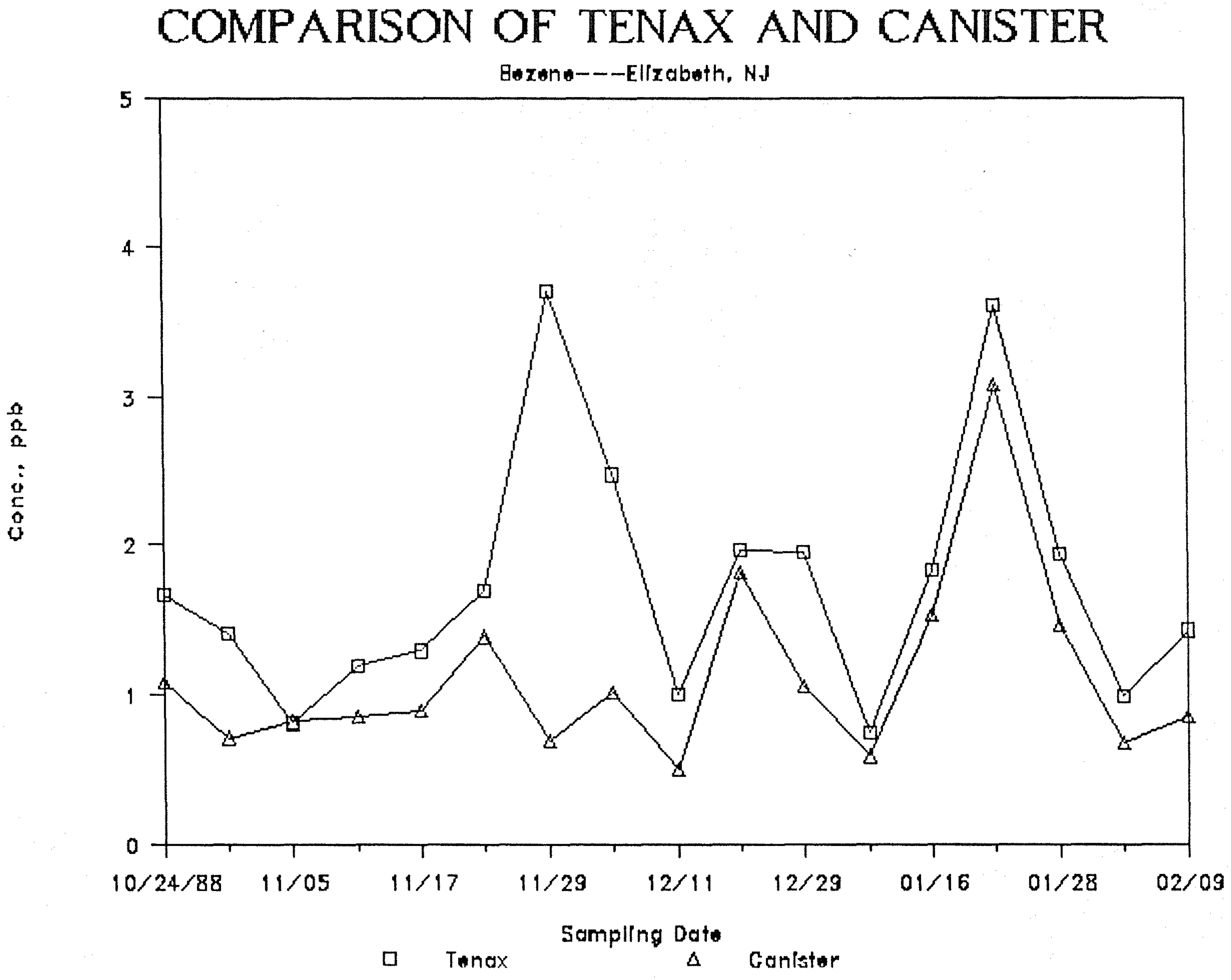


Figure 4.13 Concentration plots of BZ, Elizabeth site

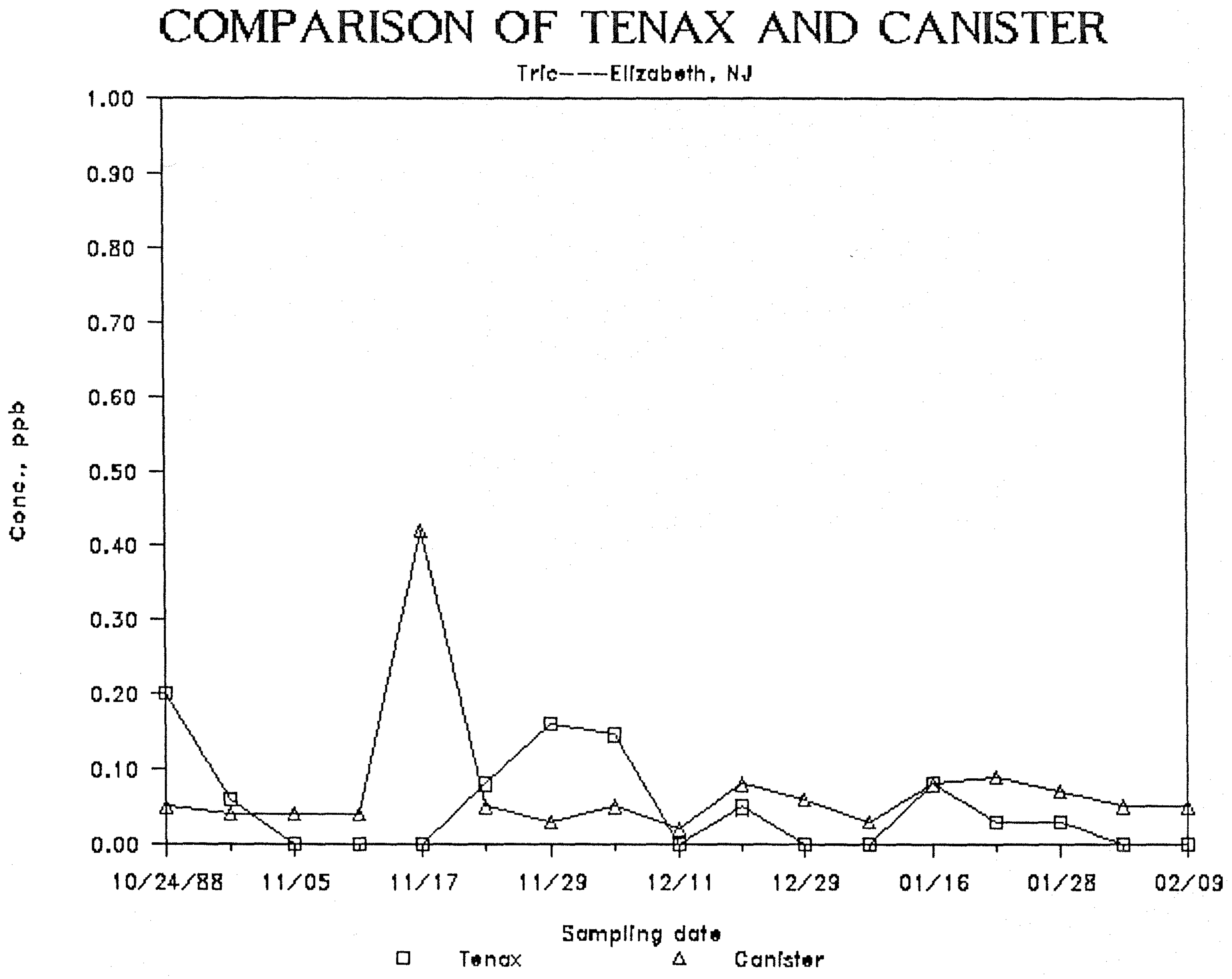


Figure 4.14 Concentration plots of TRIC, Elizabeth site

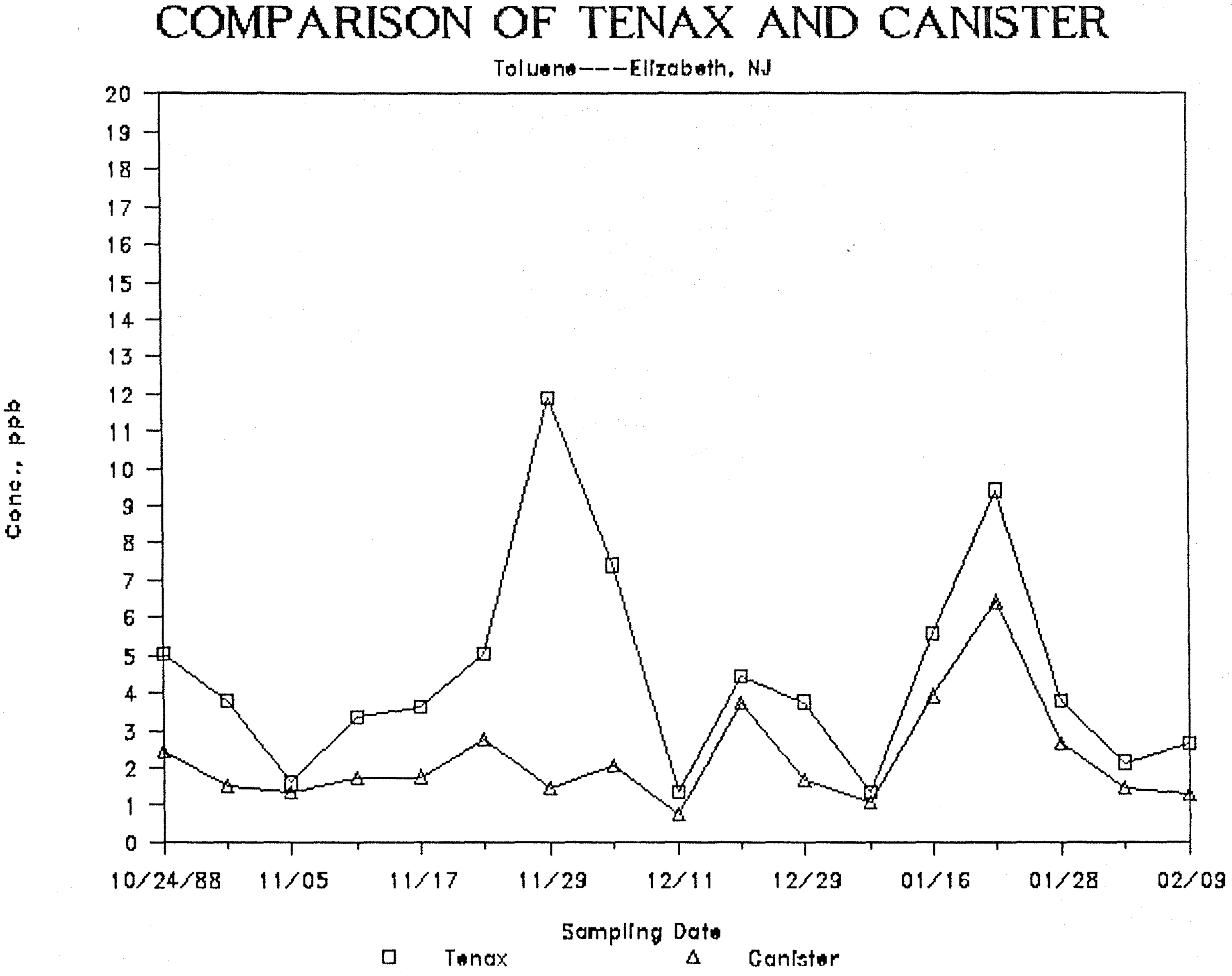


Figure 4.15 Concentration plots of TOL, Elizabeth site

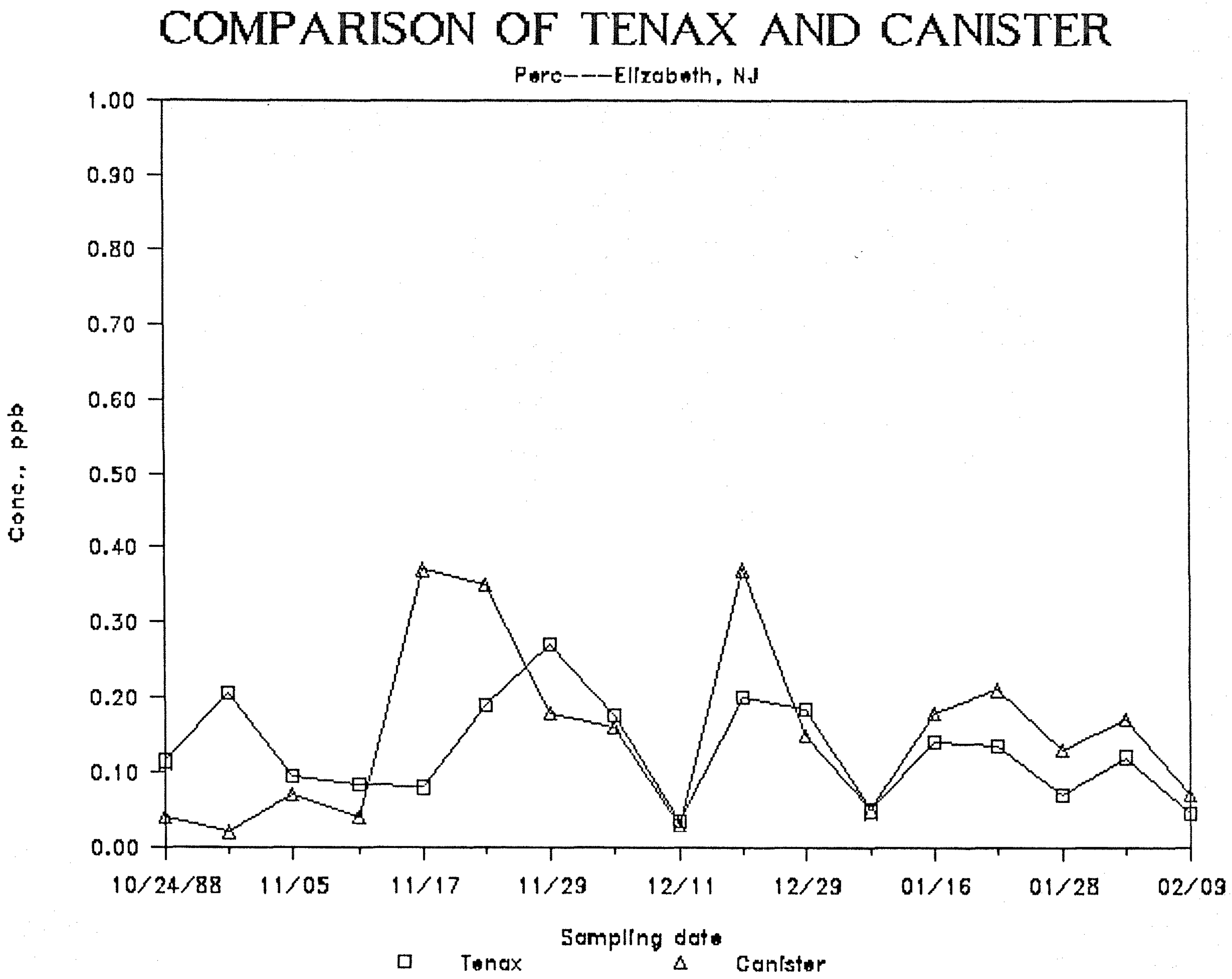


Figure 4.16 Concentration plots of PERC, Elizabeth site

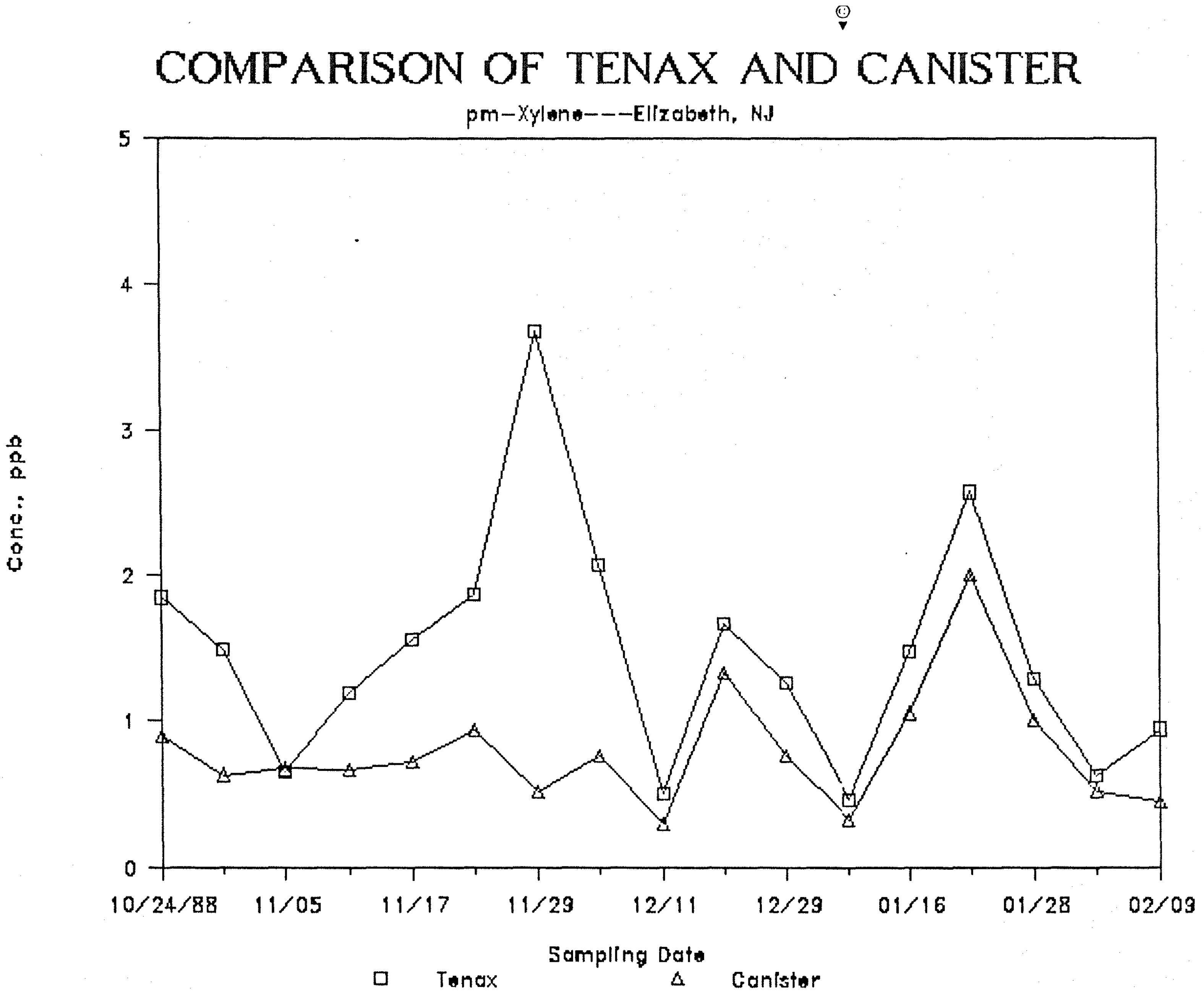


Figure 4.17 Concentration plots of PMX, Elizabeth site

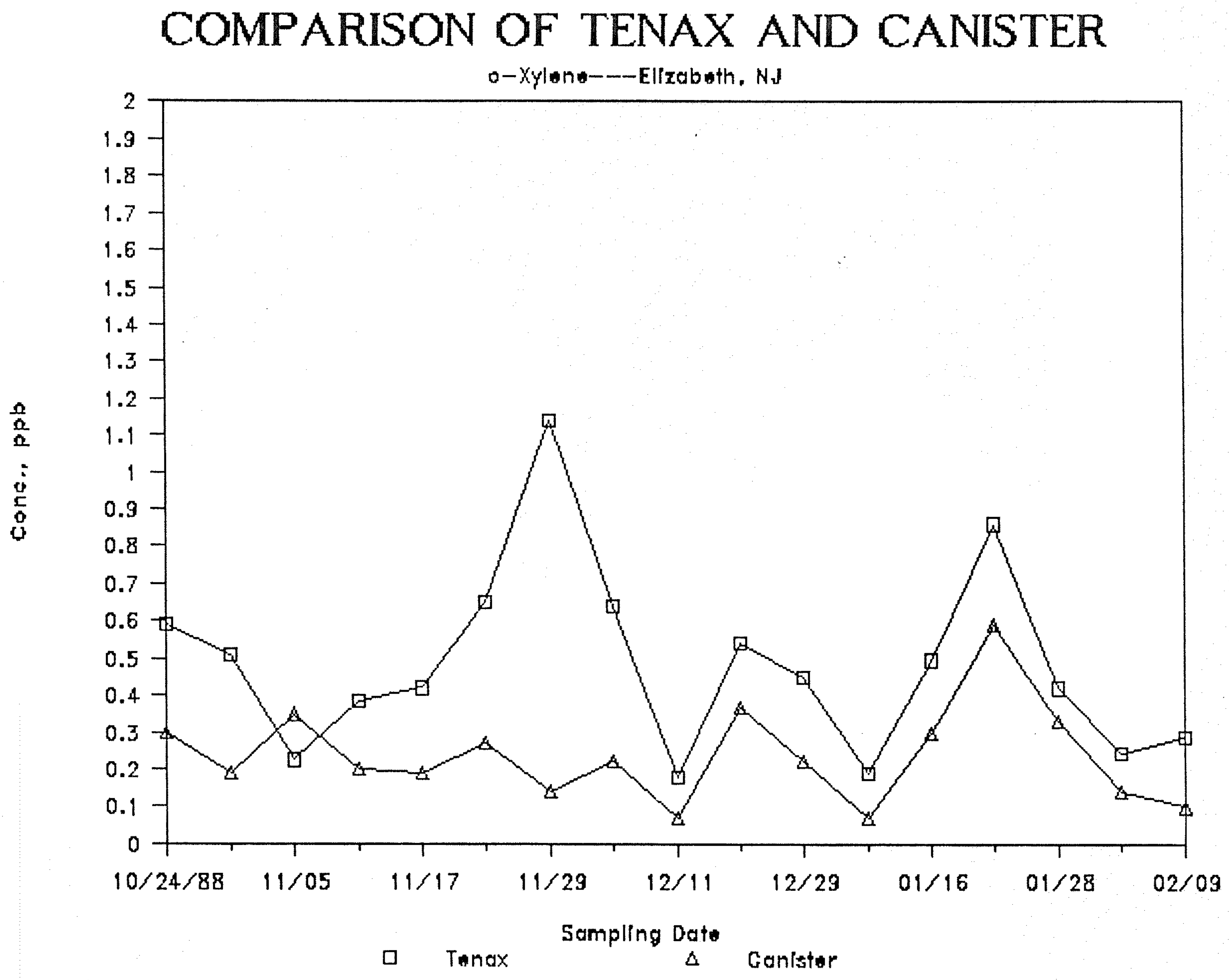


Figure 4.18 Concentration plots of OX, Elizabeth site

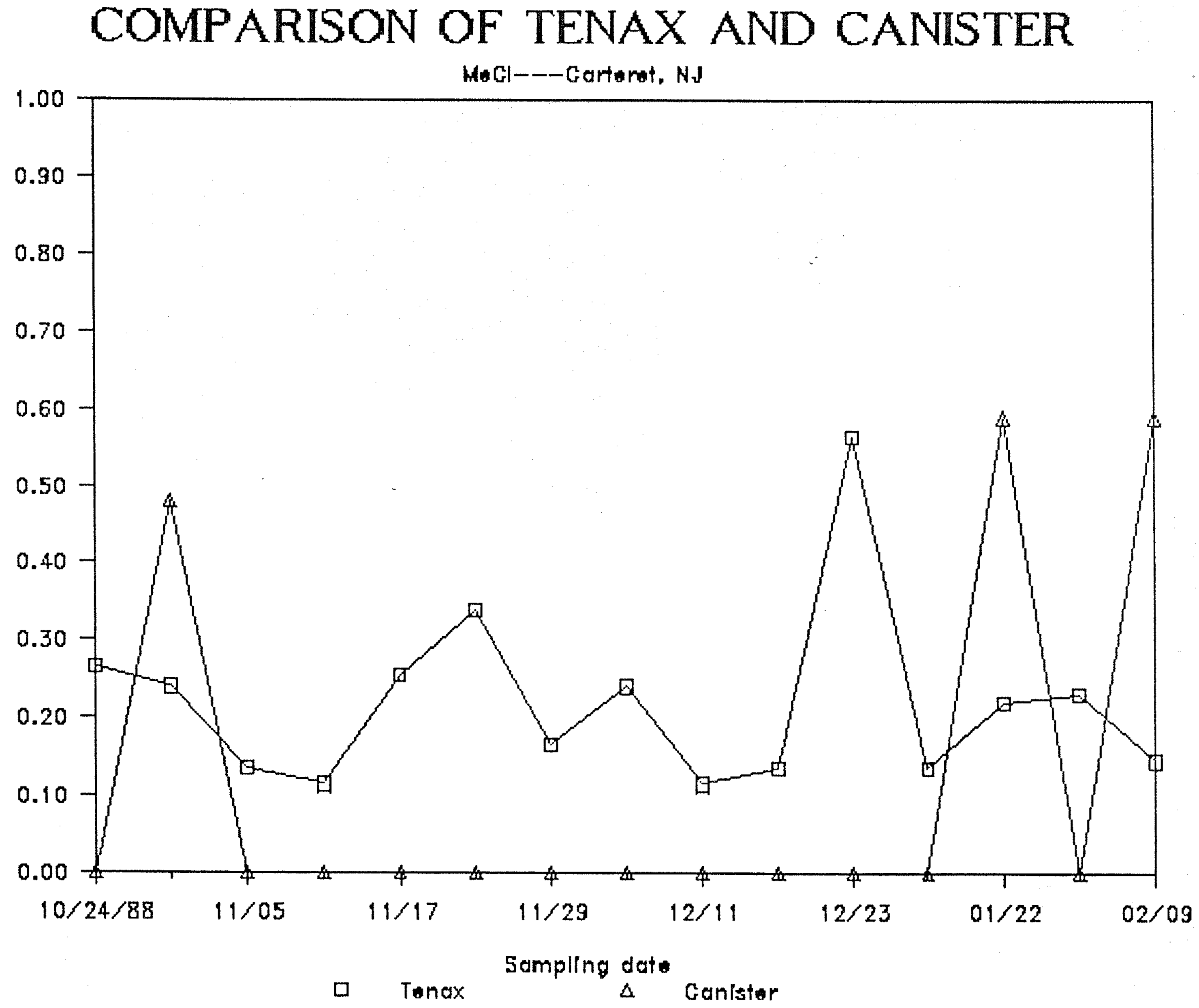


Figure 4.19 Concentration plots of MECL, Carteret site

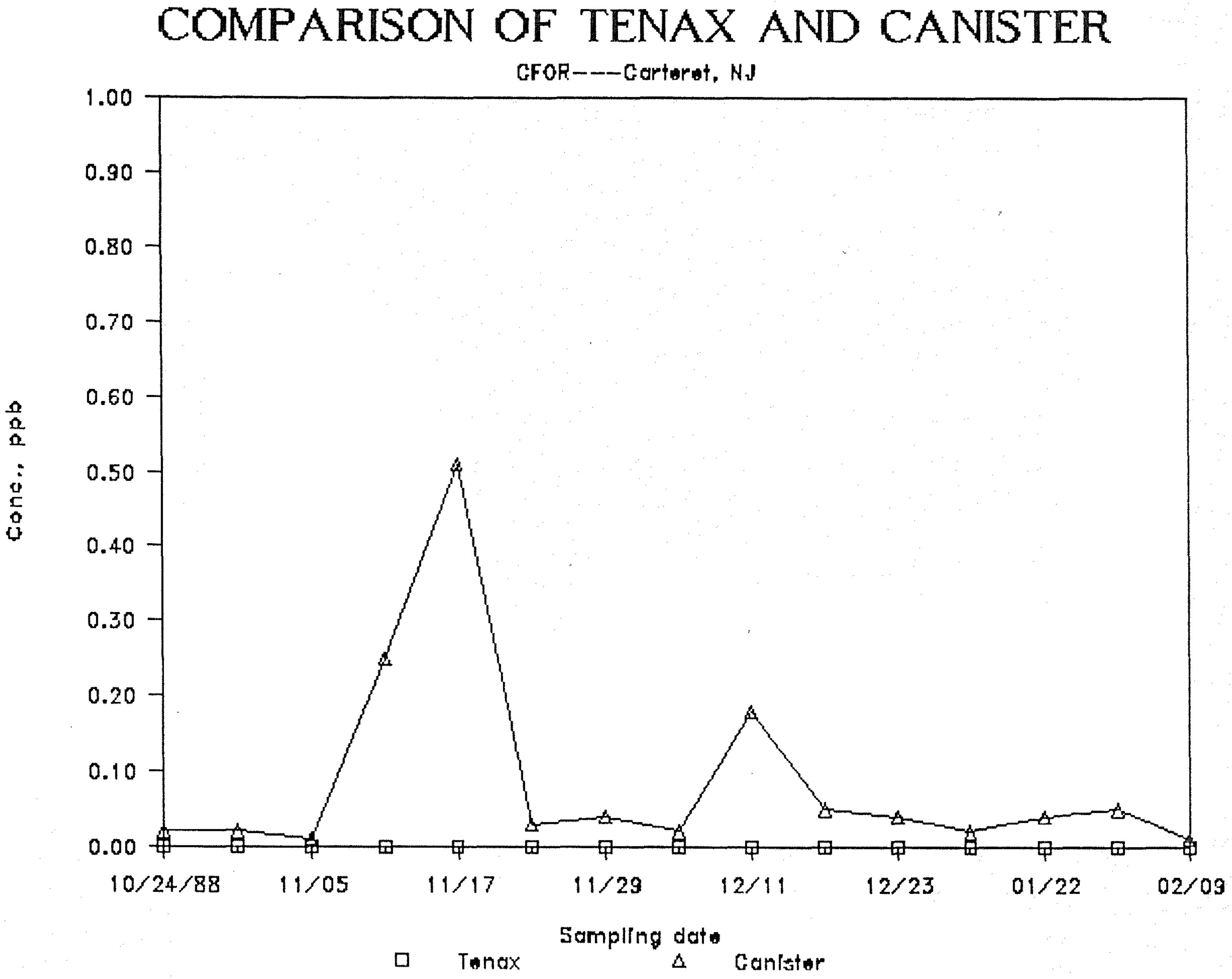


Figure 4.20 Concentration plots of CFOR, Carteret site

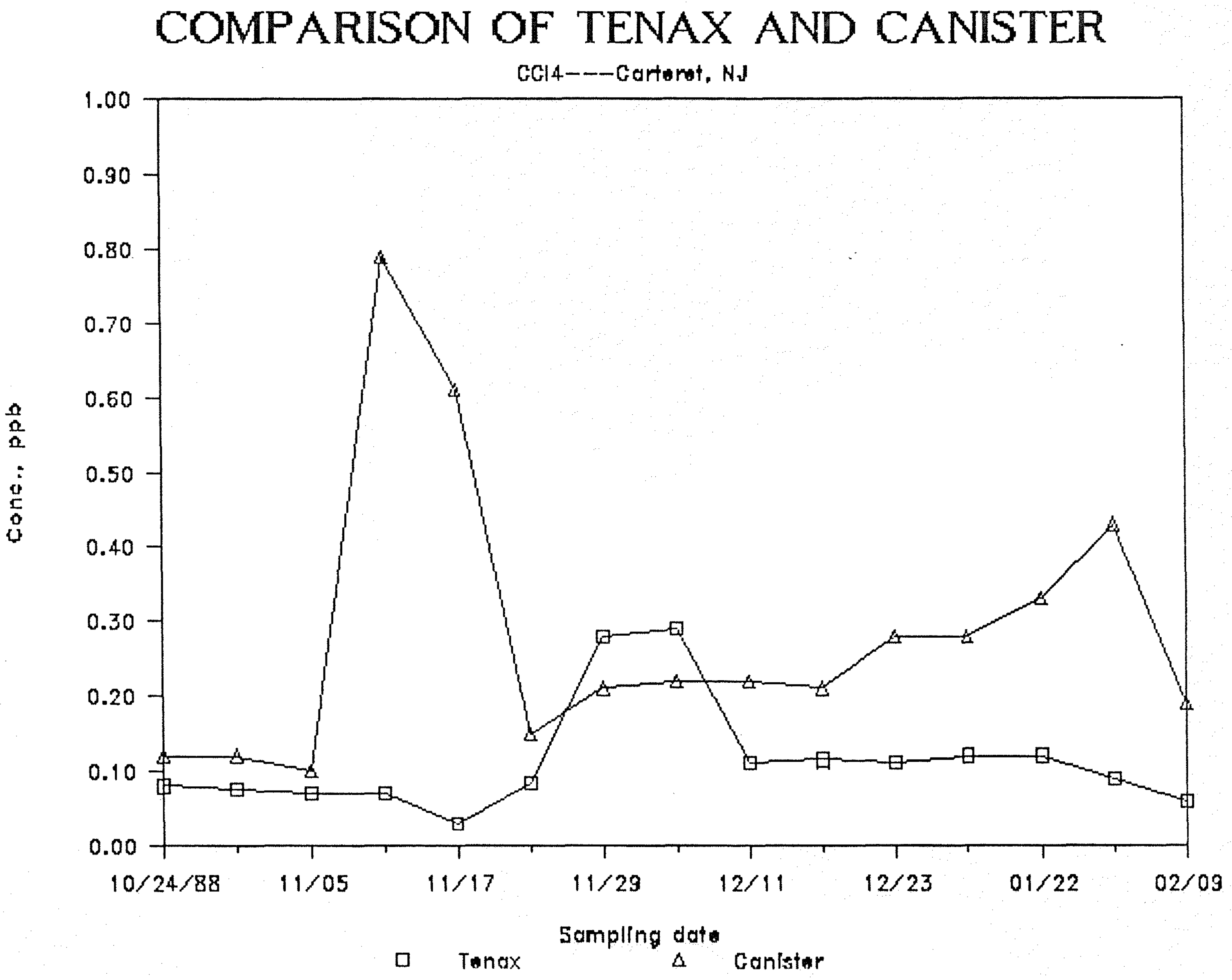


Figure 4.21 Concentration plots of CCL4, Carteret site

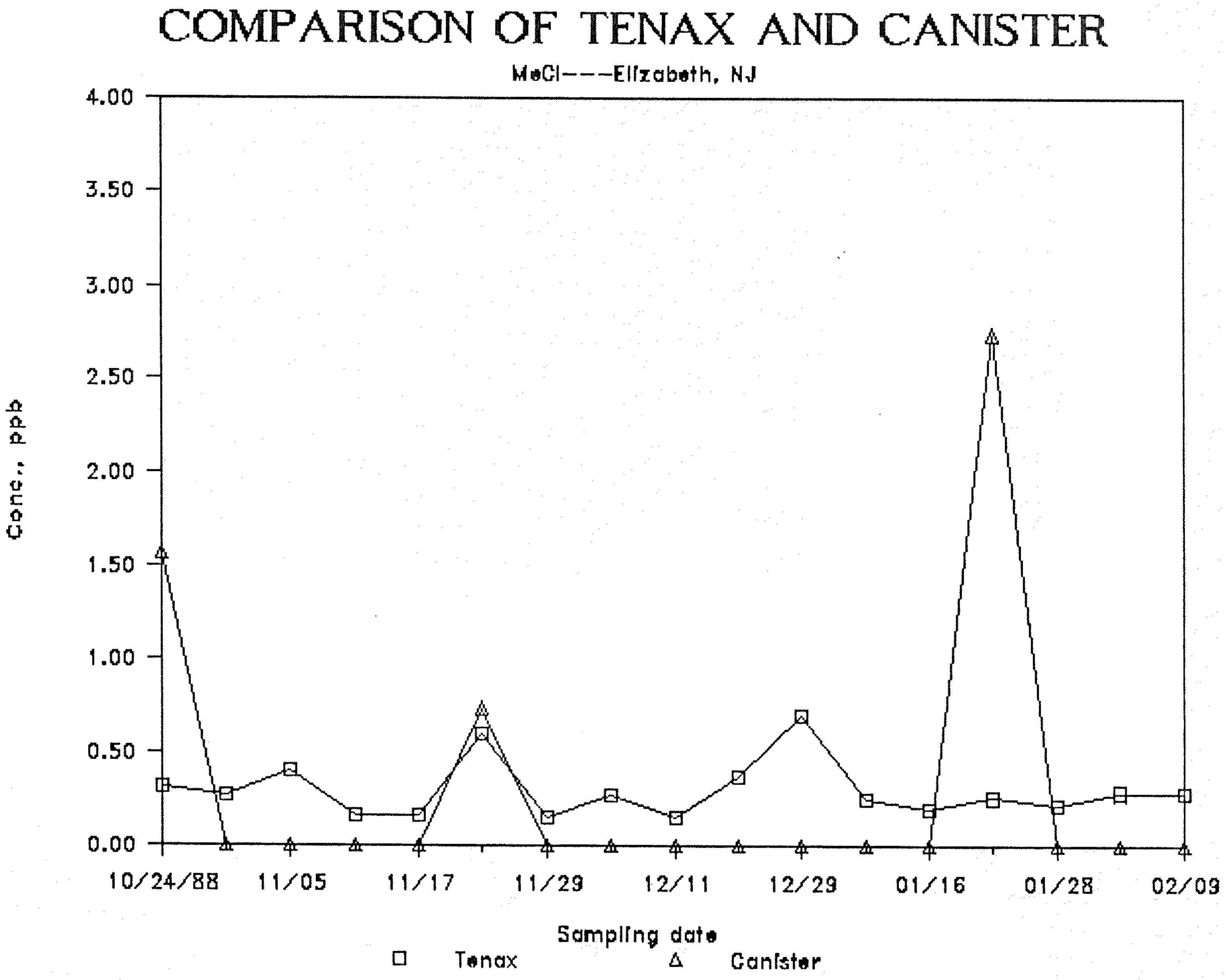


Figure 4.22 Concentration plots of MECL, Elizabeth site

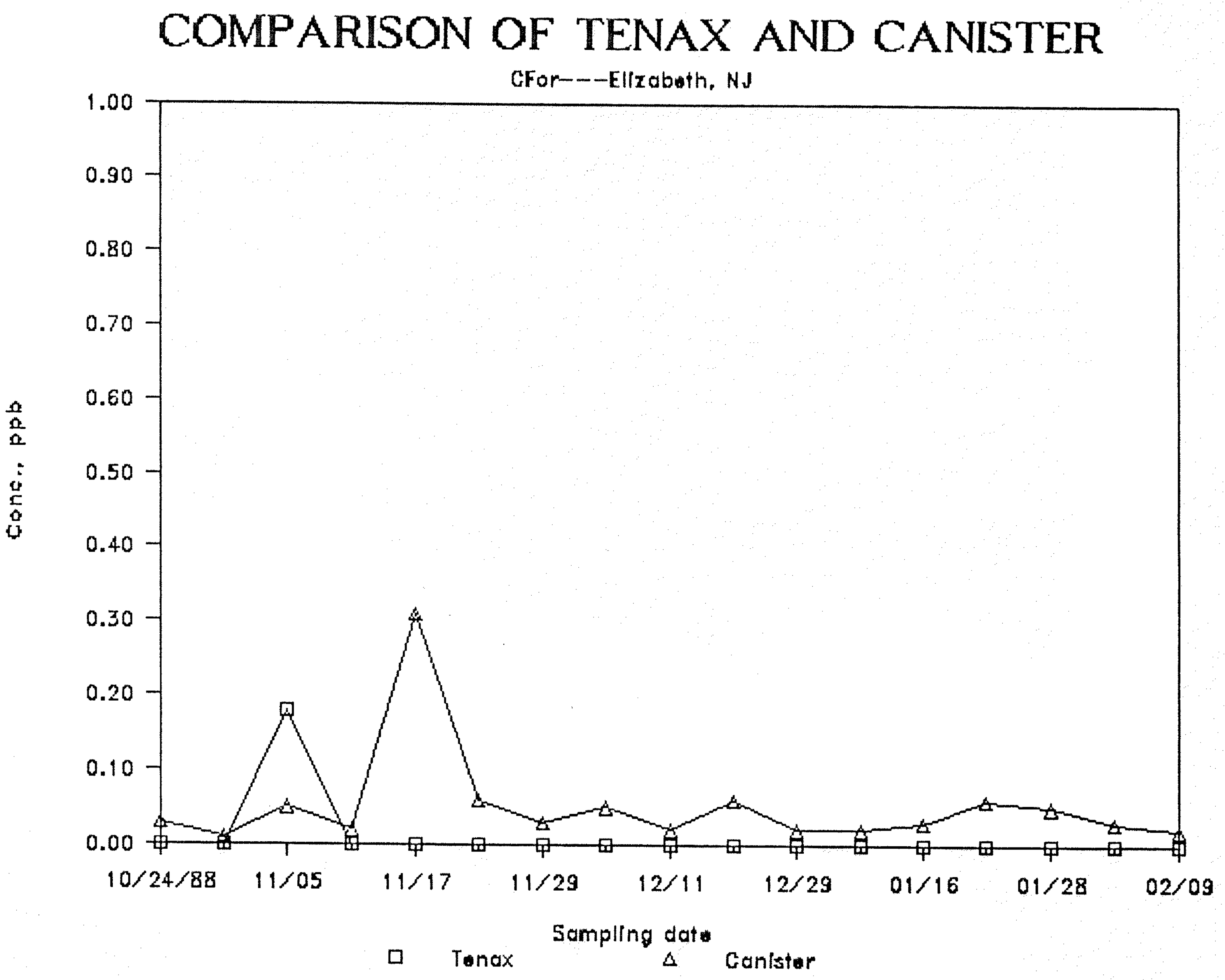


Figure 4.23 Concentration plots of CFOR, Eliabeth site

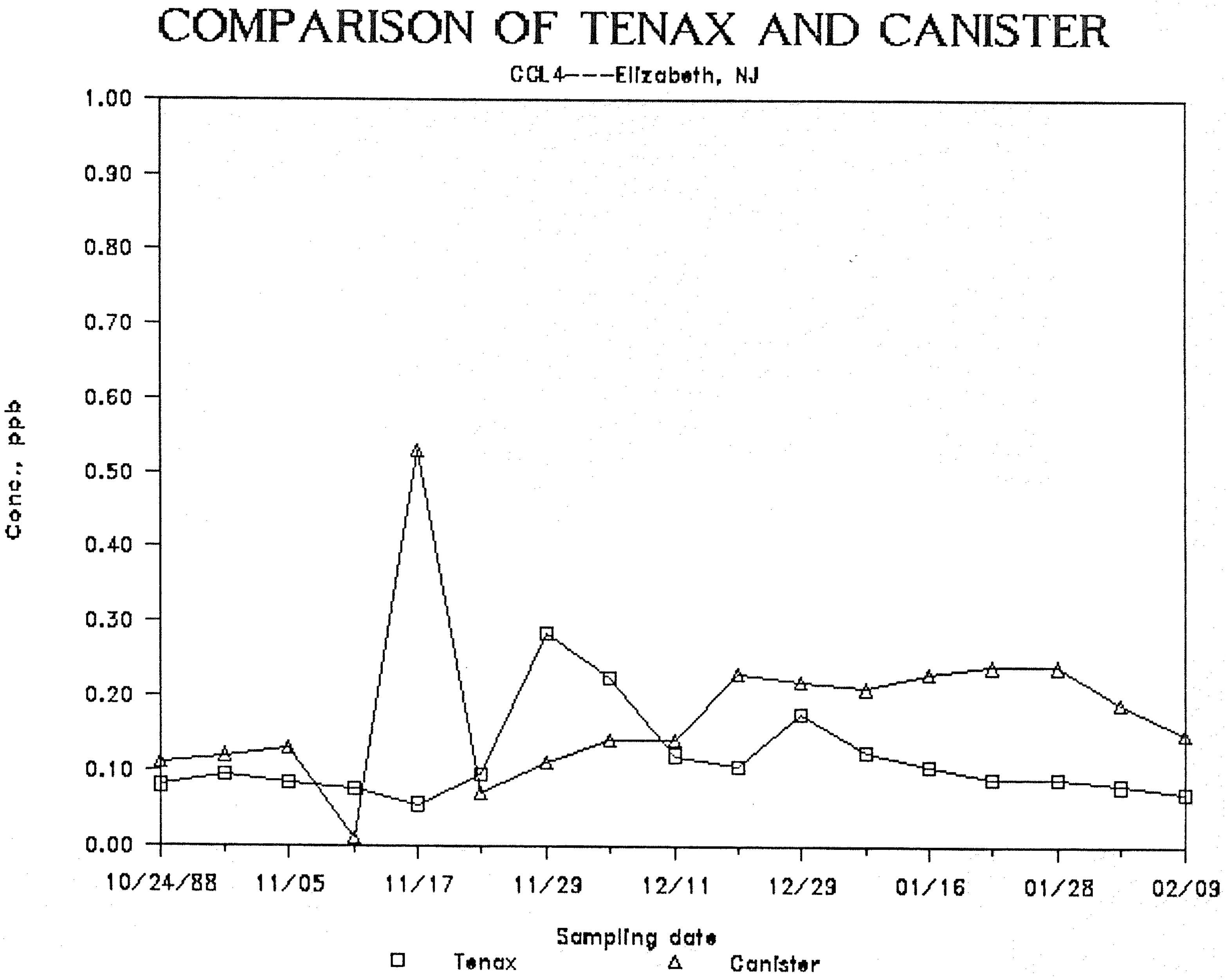


Figure 4.24 Concentration plots of CCL4, Elizabeth site

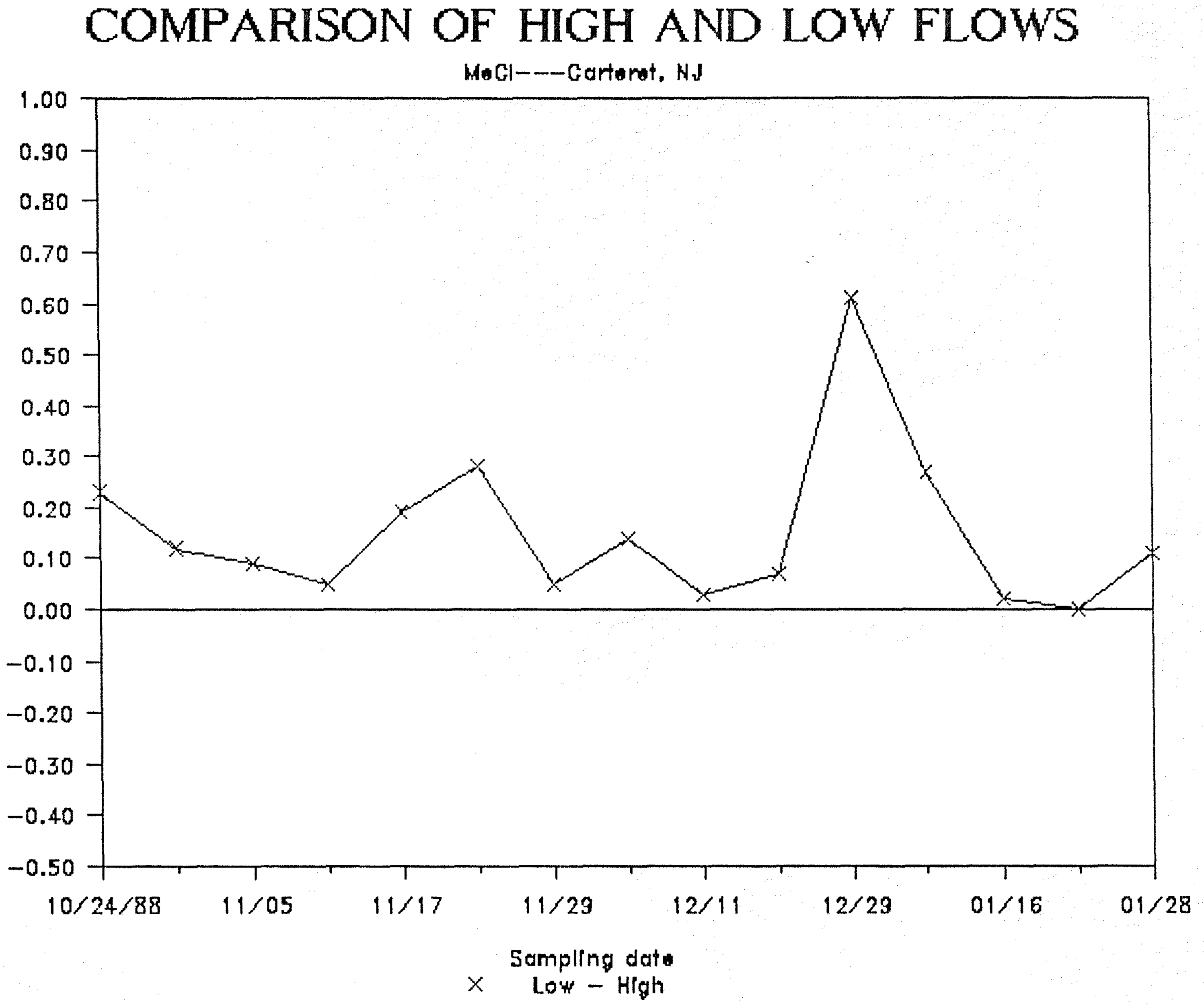


Figure 4.25 Comparison between high and low flow tubes, for MECL at the Carteret site

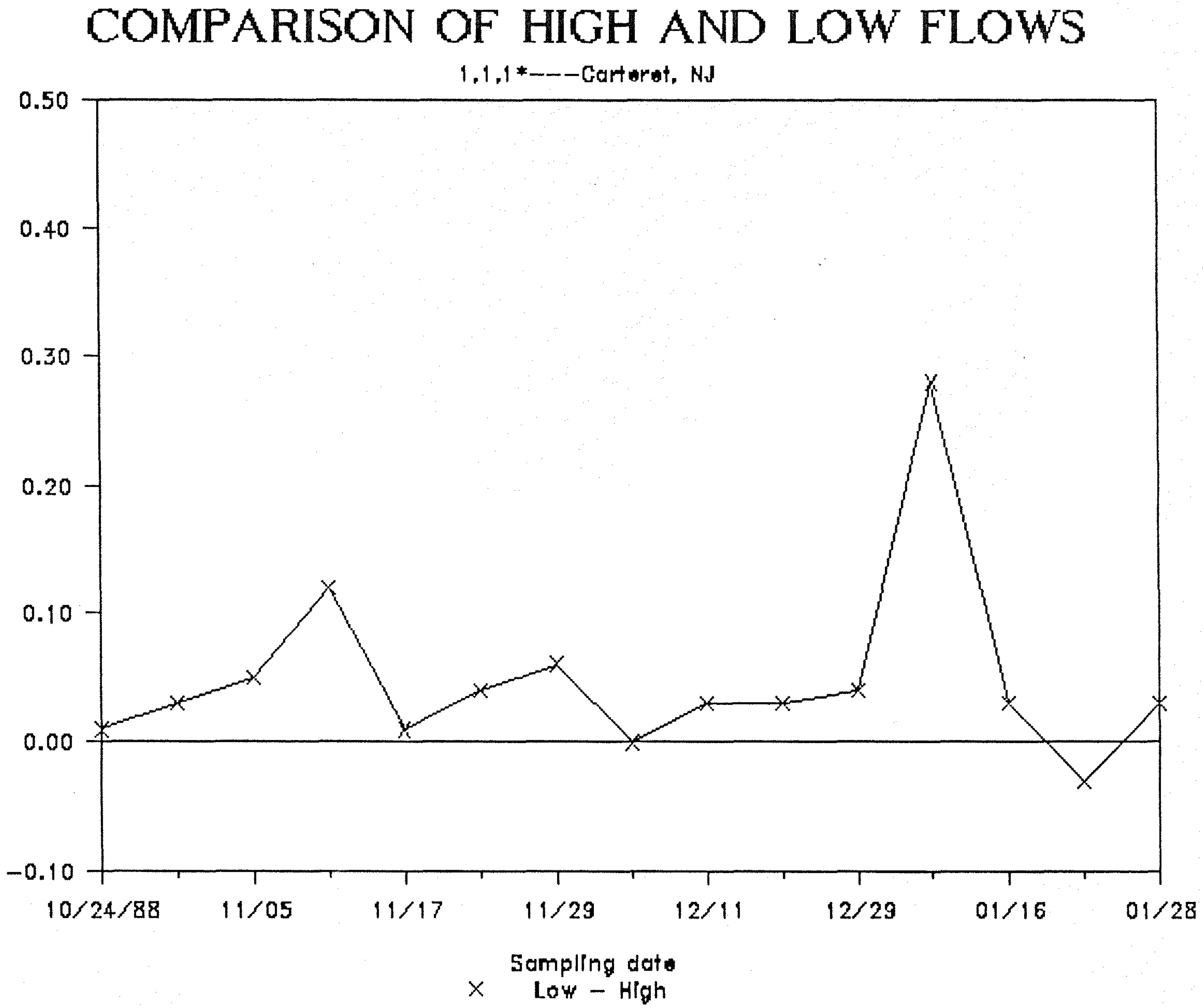


Figure 4.26 Comparison between high and low flow tubes, for 111* at the Carteret site

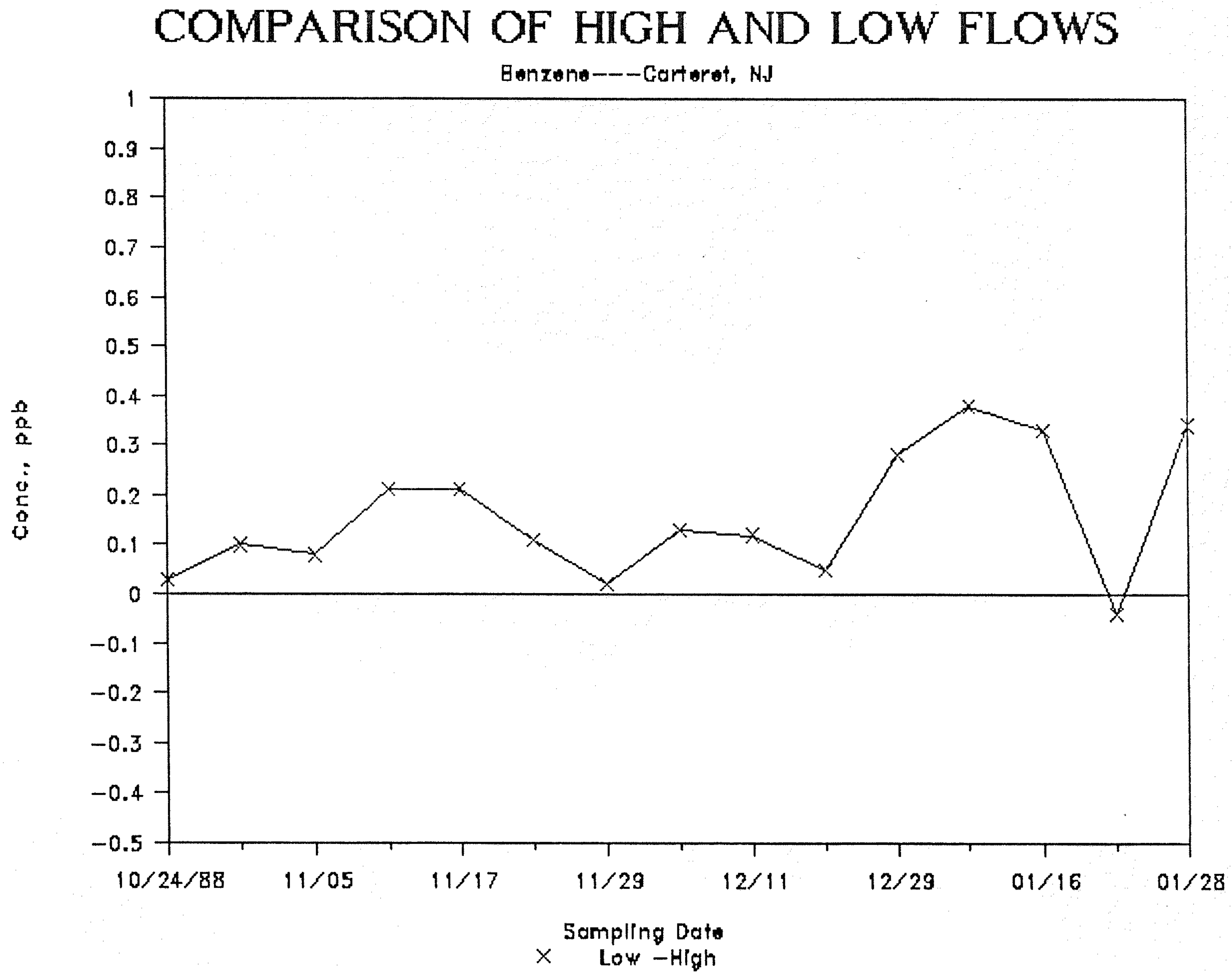


Figure 4.27 Comparison between high and low flow tubes, for BZ at the Carteret site

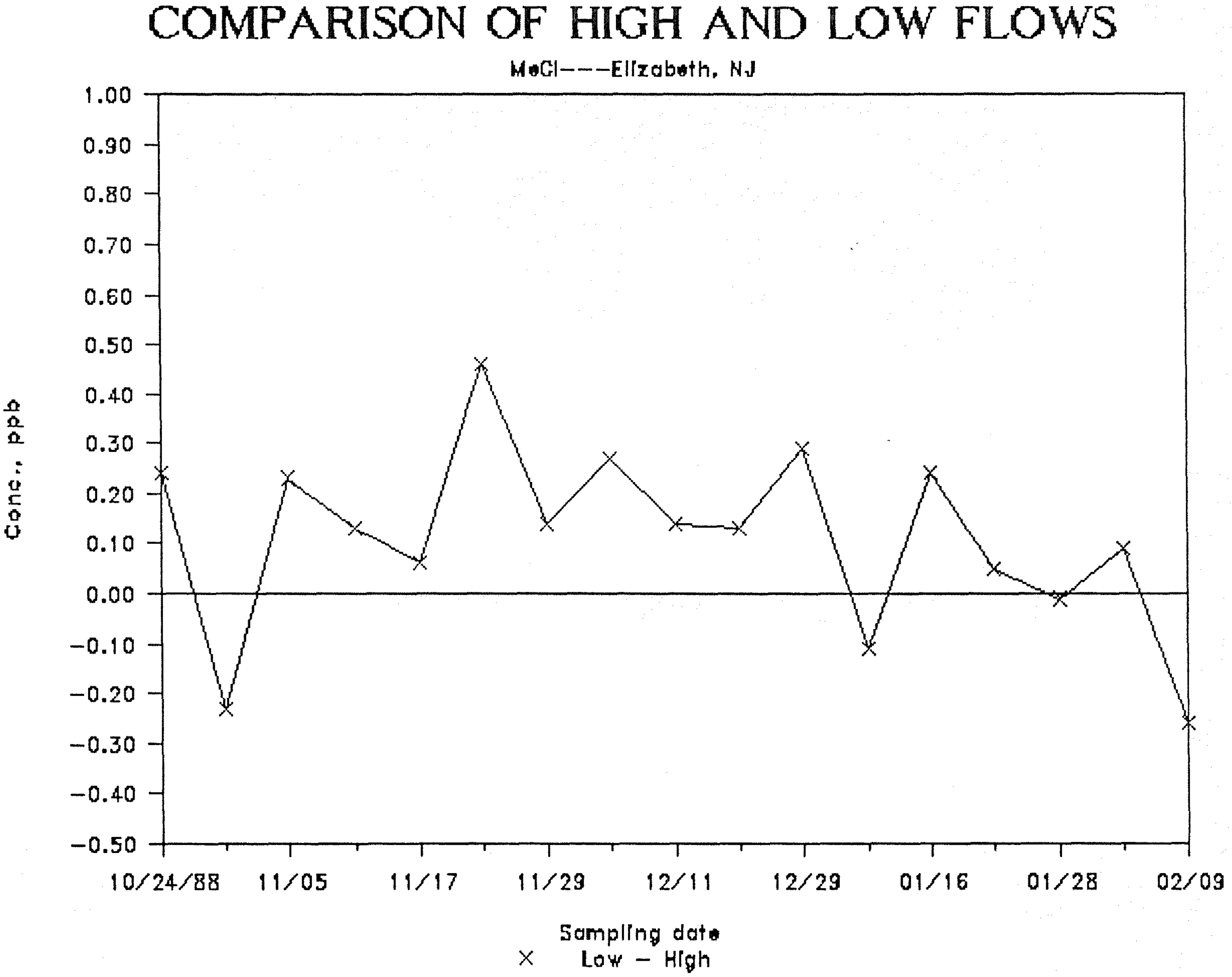


Figure 4.28 Comparison between high and low flow tubes, for MECL at the Elizabeth site

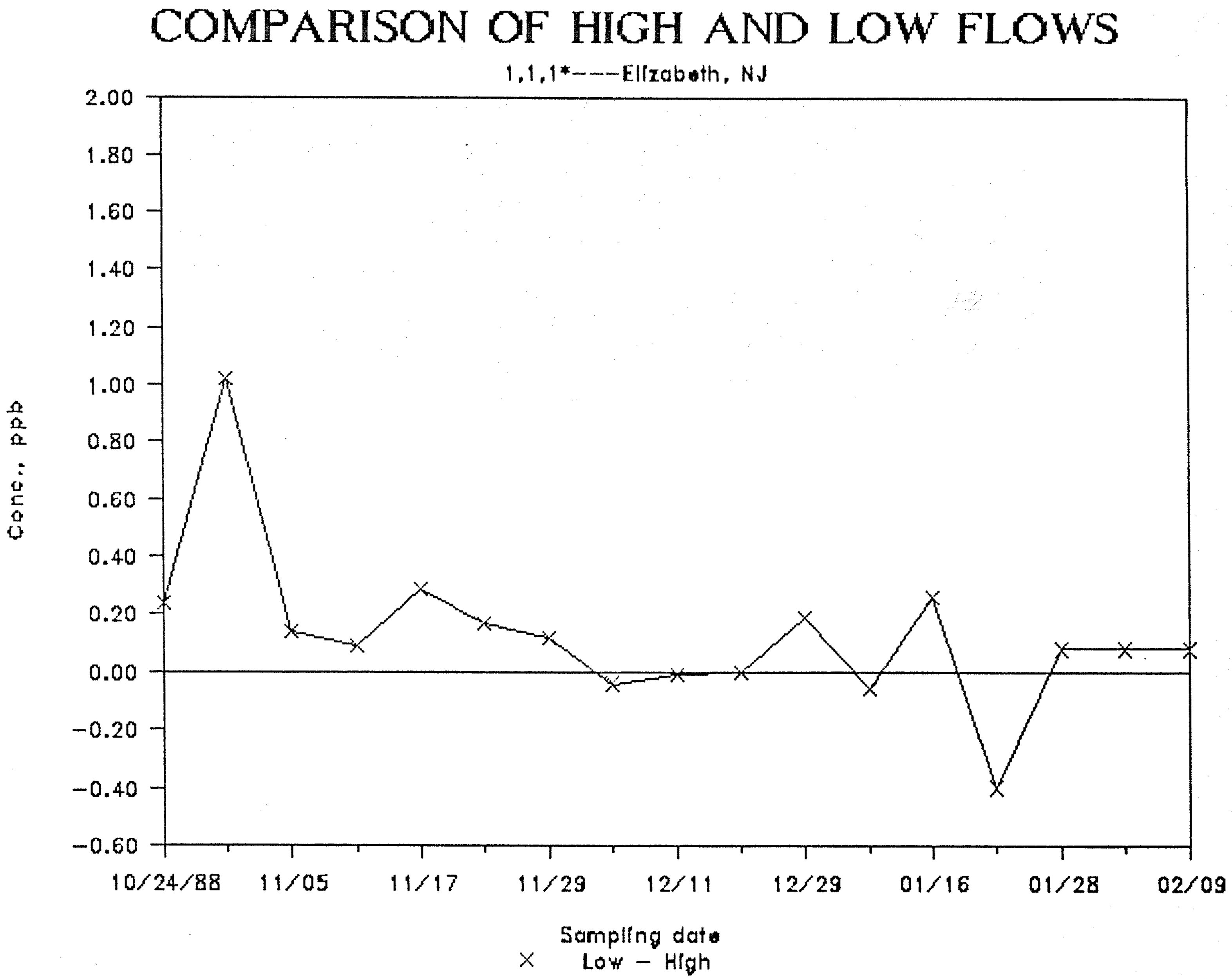


Figure 4.29 Comparison between high and low flow tubes, for 111* at the Elizabeth site

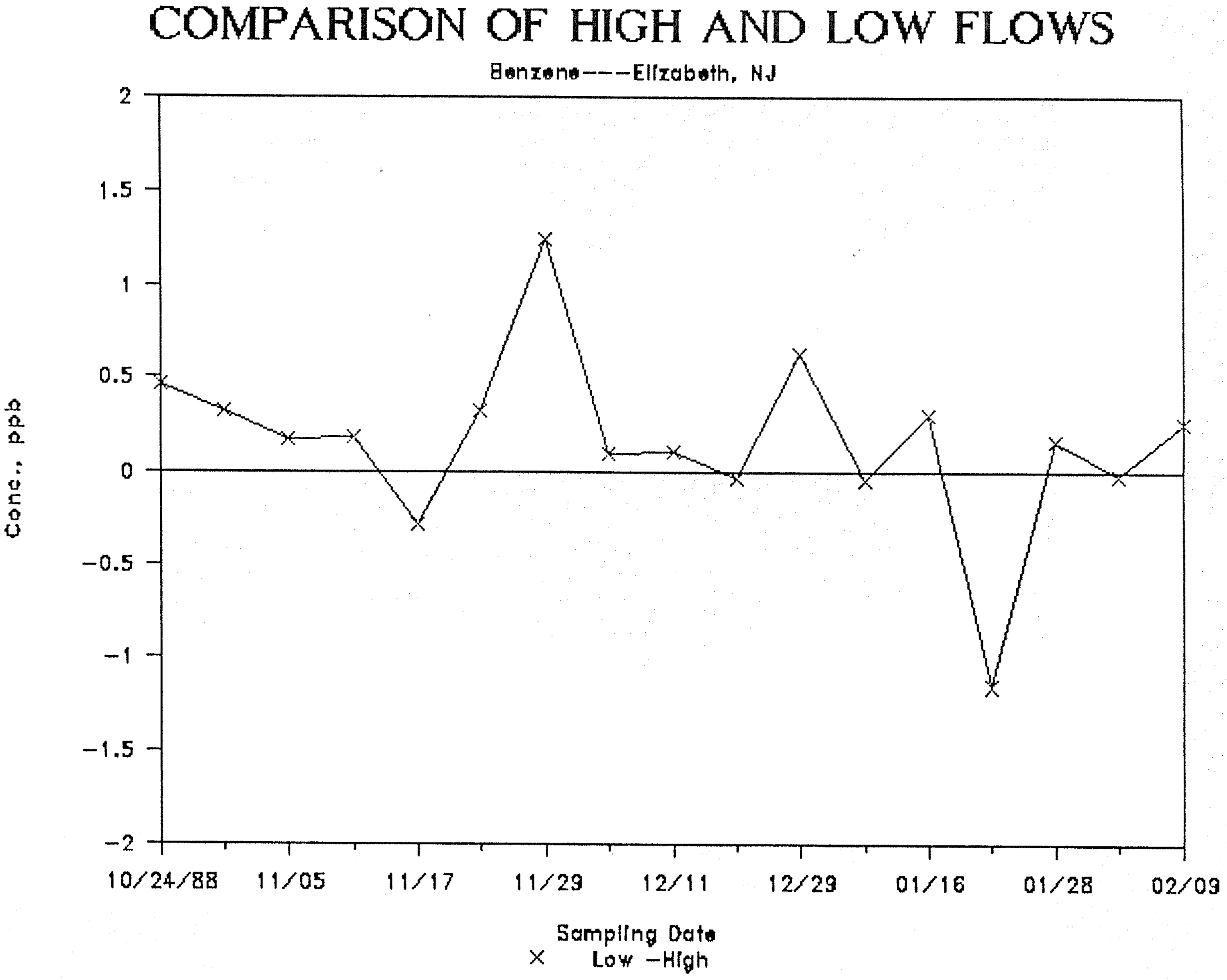


Figure 4.30 Comparison between high and low flow tubes, for BZ at the Elizabeth site

5. CONCLUSIONS AND DISCUSSION

Both the Tenax trap method and the Canister Collection method are considered reliable, with the average recovery efficiencies of 98.35 % and 95.51 %, as well as the average relative standard deviations of 8.42 % and 9.12 % correspondingly.

Tenax-GC has been known for its low water affinity, i.e., unlike the Canister collection system, the impact of water vapor upon the analysis is insignificant [20]. The Tenax traps can be reused for numerous cycles, as long as employed in normal duty and under the temperature limit. Heavy usage will cause the textures of the polymer beads to become looser and the surfaces fluffy [11]. In such condition, the adsorption ability is much diminished; and irreversible adsorption and decomposition of the polymer beads may occur, consequently erroneous analytical results are yielded. Therefore, checking for deteriorated Tenax-GC should be routinely carried out for reused traps before sampling.

In order to prevent background formations, more care should be exercised while handling the traps, and a thorough check of the carrier gas purity, the tubing connections and all the joints, etc., should be performed.

The Canister collection method is regarded as fairly good and of great potential, for many obstructions to wider applications have been tackled. Sample integrity and storage stability [8,9], clogging by CO_2, frost, and unfavorable water vapor effects have been addressed, and the attempt to automate the method has progressed substantially so far. It is promises to succeed in the near future.

Moreover, by utilizing the whole air samples collected in the Canisters, one can develop diverse analytical methods for comparison studies, because the samples are collected without selectivity due to any adsorption medium, and are free of backgrounds or artifacts from the adsorbent.

As for the losses in recoveries for PMX and OX, they can be improved by simply raising the temperature in the transfer line to 80 ^{o}C or slightly higher. It can be obviously seen in Figure 4.02 that the tranfer rates remain essentially the same at temperatures 80 ^{o}C and higher. Yet if the line temperature is heated near or at 100 ^{o}C, water vapor will be delivered along with the revaporized VOCs to the precolumn, and will cause plugging.

It may be concluded that both the Tenax trap method and the Canister collection method are useful, valuable and are worth more efforts in their improvement.

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