

Technical Completion Report
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IDENTIFICATION OF TOXIC COMPONENTS IN OIL REFINERY EFFLUENTS
AND DETERMINATION OF THEIR EFFECT UPON
THE AQUATIC BIOTA

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PROJECT COMPLETION REPORT

OWRR - B - 017

Analyses of Toxic Compounds in Oil Refinery Effluents and Determination
of Their Effects Upon the Aquatic BiotaOutline

- I. Introduction. General discussion of objectives, procedures and significant results.
- II. Materials and Methods
 - A. Source of samples. Problems in preserving samples
 - B. Bioassay
 1. Daphnia
 2. Fathead Minnows
 - C. Extraction procedures
 1. Solvent
 2. Activated carbon
 3. Flash evaporation
 - D. Analytical
 1. Atomic absorption
 2. Ion probe
 3. Gas chromatograph
- III. Results and Discussion
 - A. Fractions collected
 1. Solvent
 2. Carbon
 3. FEV } Tables
 - B. Bioassays
 1. Daphnia
 2. Fathead Minnows
 - C. Analyses
 1. GC-MS
 2. Ion probe
 3. AA
- IV. Appendix

I. Introduction

This report summarizes results obtained July 1, 1970 to June 30, 1972 on grant, B - 017 OKLA. The objectives of the research project were:

1. to isolate and identify toxins in oil refinery effluents, and
2. to determine ecological effects upon aquatic biota.

Toxic organic fractions were isolated from oil refinery effluent samples by solvent extraction (hexane, methylene chloride, and toluene), adsorption on activated carbon, and flash evaporation. Toxicity of extracted fractions and effluent samples was determined by microbioassays with Daphnia magna. Fish bioassays were performed with fathead minnows (Pimephales promelas) to determine the 48 hr median tolerance level (TL_{M48}) of the effluents.

Analyses of toxic organic fractions were performed with gas-liquid chromatography to resolve the complex mixtures of compounds. Demonstrably toxic fractions which could be chromatographically resolved were identified by combination gas chromatography - mass spectrometry. Analyses of toxic heavy metals in the effluents were performed by atomic absorption spectrophotometry. Specific ion electrodes were used to determine ammonia, chloride, fluoride, and sulfide concentration in the effluents.

Uptake of toxins by fish was measured by atomic absorption analyses of the heavy metals content of the fish. Organic compounds were extracted from the exposed fish by steam distillation-ether extraction and chromatographed to compare with extracts from the effluents.

The oil refining industry, like many other industries, is faced with major waste disposal problems. When water is contacted with crude oil, distillation fractions, or refined products the water dissolves

some of the organic compounds and forms emulsions with others. Most of the emulsified organics are removed by primary treatment, i.e., API trap or air flotation. The dissolved organic compounds and some residual emulsified compounds, however, are more difficult to remove satisfactorily for discharge to the receiving stream. Most refineries use some type of biological treatment to remove these dissolved and emulsified organics.

Biological degradation removes 40 to 60% of the organic compounds from oil refinery effluents, as measured by the chemical oxygen demand (COD) test. The remaining COD is composed of biologically-resistant organic compounds, ammonia, and miscellaneous biocides and additives which make the task of cleaning up oil refinery waste waters difficult. Oil refinery effluents are extremely complex and potentially may contain water soluble compounds originally present in the crude oil as well as additional compounds formed or added in the refining process. If the chemical composition of the waste waters were known, more effective waste treatment methods could be devised. Some compounds such as dimethyl naphthalenes (Brady 1968), polynuclear hydrocarbons (Wedgewood and Cooper 1953, 1954), and 1-hexanol (Sugar and Conway 1968) have been positively identified in oil refinery or petrochemical effluents. Other compounds have been detected by GLC retention time (Sugar and Conway 1968; Cochran and Bess 1966) but not positively identified. The complexity, trace concentrations, and low volatility of the organic compounds have been major obstacles to chemical analysis of refinery effluents.

We have used continuous steam-distillation ether extraction as a technique for isolating relatively volatile organic compounds from oil refinery effluents. A combination gas chromatograph - mass spectrometer was utilized for analysis of the steam volatile extract. We have

identified a homologous series of aliphatic hydrocarbons from undecane through octadecane (Burks 1971). Since these hydrocarbons are normal constituents of crude oil their presence in the waste waters which had been in contact with the crude oil was not unexpected. However, the presence of these hydrocarbons in final effluents after biological treatment indicates either preferential substrate utilization by bacterial sludge organisms or more resistance to biodegradation by long straight-chain hydrocarbons than was previously expected.

Some organic compounds containing tertiary carbons are known to be resistant to biodegradation (Davis 1967). Less than 20% of the compounds o-chloro-nitro-benzene, tertiary butylbenzene, and phenyl ether were degraded by acclimated sludge organisms during 75 days continuous exposure (Ludzack and Ettienger 1963). Fifty to 80% of the oil in a highly aerated system was degraded in the first week at 25° C (Ludzack and Kinkead 1956). Approximately 10% of the oil had not been degraded after 30 days aeration.

Water is used to "de-salt" crude oil at the refinery and dissolves many compounds from the crude oil. The solubility of aliphatic hydrocarbons in water is quite low, but other heteroatomic compounds containing oxygen (such as phenols) may be highly soluble. Crude oil composition is variable depending upon the geological strata and geographical location of the source (Bestougeff 1967) (Table 1).

Since the previously identified aliphatic n-hydrocarbons in the C₁₁H₂₄ to C₁₈H₃₈ range are relatively easily degraded, but persist in final effluents, it seems likely that more resistant compounds such as tertiary branched hydrocarbons and highly substituted aromatic hydrocarbons also are persistent in final effluents.

It has been demonstrated that oil refinery final effluents cause acute deleterious effects to fish and other aquatic organisms (Turnbull,

Table 1. Types of compounds in crude oil*

Class	Range of percent in crude oil
Aliphatic <u>n</u> -hydrocarbons	
Straight Chain	
C ₅ - C ₁₀	11.5
C ₁₁ - C ₂₀	10.3
C ₂₁ - C ₃₀	2.23
C ₃₁ - etc.	0.25
Branched Chain	
C ₆ - C ₁₀	6.7
C ₁₁ - C ₁₂	1.7
C ₁₃ - C ₁₇	2.3
C ₁₈ - C ₂₅	1.42
C ₂₆ - C ₃₈	0.83
Cyclo paraffin hydrocarbons	30 - 60
methyl cyclohexane	2.7
Aromatic hydrocarbons	
monocyclic	
polycyclic	<1%
Naphtheno - aromatic hydrocarbons	
Resins	
Asphaltenes	0 - 20
Heteroatomic compounds	
Sulfur compounds	1 - 40
Nitrogen compounds	0.01 - 0.2
Oxygenated compounds	.06 - >1%
phenols	<0.1%
acids	
Metallic compounds	0.01 - 100**

* Summarized from Bestougeff, 1967.

** mg/liter

DeMann, and Weston 1954; and Hood, Duke, and Stevenson 1959). Many of the compounds known or suspected to occur in oil refinery effluents, i.e., phenols, cresols, etc., are acutely toxic to aquatic organisms (Wolf and McKee 1964; and Pickering and Henderson 1966).

Some highly treated oil refinery effluents may not be acutely toxic, but exhibit long-term chronic toxicity (Graham and Dorris 1970). Graham found that chronic toxicity appeared to be reduced during periods when the catalytic cracking tower was not in operation. Catalytic cracking is used to convert low octane naphtha type compounds into high octane aliphatic and aromatic hydrocarbons. Some partially oxidized fragments, such as phenols, are formed in the hydro-cracking process and are dissolved in contact wash waters. These compounds are highly toxic to aquatic organisms. Further knowledge of the chemical composition of process and final effluents is expected to aid in predicting the quality of waste water and the effect upon aquatic life of discharges from oil refinery effluents.

II. Materials and Methods

A. Source of samples

The members of the Oklahoma Oil Refiners' Waste Control Council have submitted water samples for bioassay to the Oklahoma State University Reservoir Research Center for several years. Final effluent, process effluent, and receiving stream water samples are collected by refinery personnel as 24 hr composite samples. The samples are shipped in polyethylene carboys or disposable polyethylene bags (5 gallons). Special preservatives are not added to the samples.

The samples are subjected to fish toxicity bioassay, organic analysis, and heavy metal analysis. Samples for organic analyses are

solvent extracted, filtered through activated carbon, or flash-evaporated. Samples for heavy metal analyses are collected in 8-ounce polyethylene bottles and acidified to pH 2 with 2 M nitric acid.

B. Bioassay

The fish acute-toxicity bioassays are performed with fathead minnows purchased from local bait dealers who obtain fish from Minnesota. Minnows are acclimated for 7 to 14 days prior to bioassay. Water used for dilution and holding fish is de-chlorinated by de-ionization and stored. The de-chlorinated water is passed through 2 activated carbon columns in series prior to use for dilution (Table 2).

Acute toxicity bioassays are performed in 5 gallon polyethylene buckets, submerged in a water bath to maintain uniform temperature (Fig. 1). Total volume of the test solution is 3.7 gal. The static bioassay originally was conducted for 48 hr, but later was extended to 96-hr.

Continuous-flow 30-day toxicity fish bioassays have been performed on-site at a cooperating refinery. Treated effluent was pumped through activated carbon columns (3" x 18") or an acclimated activated sludge unit prior to passing through the test aquaria. Test minnows were spawned and raised in our laboratories and were of known age and condition. Ten gallon glass aquaria were used as test containers. The fish were fed daily with Bio-rell. Dead fish were removed and frozen in individual polyethylene bags. Carbon columns were replaced at weekly intervals. The spent activated carbon was air-dried and soxhlet-extracted. Fish were examined after bioassay for histological effects and accumulation of heavy metals.

Static bioassays of solvent extracts, flash-evaporation extracts and effluent samples were performed with 20-hr old Daphnia magna in 45 ml of test solution. Initially we attempted to take the time of death as a

Table II

Chemical Quality of Oklahoma State University
Laboratory Dechlorinated Tap Water

<u>Chemical</u>	3/10/72 Measured Concentration <u>µg/l</u>	Precision of <u>Method</u>	<u>Method</u>
Sulfate	34.0	0.1	APHA, turbidimetric
Chloride	7.0	0.1	Orion specific ion electrode
Fluoride	<1.0	0.1	Orion specific ion electrode
Cyanide	<0.01		Qual. spot test, Feigel
Nitrate	4.11	0.01	Hypochlorite
Nitrite	4.02	0.01	Hypochlorite
Ammonia	2.0	0.01	Hypochlorite
Phenol	<0.1	0.1	Differential UV absorbance
Chlorine	<0.04	0.01	Iodometric, APHA
Alkalinity	158	1.0	Titrimetric, APHA
Hardness (EDTA)	168	1.0	EDTA, titrimetric, APHA
pH	8.0	±.1	pH electrode
Calcium	50.0	0.1	Atomic Absorption
Magnesium	13.0	0.1	" "
Potassium	3.0	0.1	" "
Sodium	20.0	0.1	" "
Iron	<0.01	0.01	" "
Copper	<0.005	0.001	" "
Zinc	<0.01	0.001	" "
Cadmium	<0.001	0.001	" "
Chromium	<0.01	0.01	" "
Nickel	<0.005	0.001	" "



Fig. 1. Aquaria wet room for short-term
and long-term Fathead minnow
bioassays.

measure of the relative toxicity of the sample, but changed the procedure to determining the percent of survival at 24 hr intervals (Anderson 1943).

C. Extraction procedures

Solvent extraction, adsorption on activated carbon, and flash evaporation techniques were used to isolate toxins from the refinery effluents.

Solvent extractions were performed in separatory funnels with teflon stopcock with 500 ml samples of effluent and 125 ml of solvent. Hexane, methylene chloride, and toluene were used as solvents initially, but toluene extraction was later discontinued. All solvents were Matheson Pesticide grade, certified to contain less than 10 ppt of contaminants that could interfere with electron capture gas chromatographic analyses. Solvent extracts were air-dried at room temperature in tared flasks to obtain weights of extracts. Attempts to redissolve the extracts in aqueous solutions for bioassay were not successful. The concentrated extracts tended to form droplets which could not be dissolved by aqueous solution.

Flash-evaporation of effluent samples were made with a Buchler Model FE-2C rotating flask thin-film evaporator. Approximately 10 to 25% by volume of steam plus volatile organic compounds were evaporated and condensed from 500 ml of effluent sample. The condensed steam and volatile organics were bioassayed with Daphnia magna and then extracted with methylene chloride.

Continuous-flow evaporation of ten liters of one effluent was performed. The volatile condensate was collected in 500 ml fractions which were bioassayed with Daphnia and extracted with methylene chloride. The non-volatiles and residual brines were sampled at 500 ml intervals.

The concentration of sodium, potassium, magnesium and calcium in the brine samples was measured by atomic absorption spectrophotometry.

The analysis of fish tissue and fish food for heavy metals presents special problems. The organic matrix must be converted to carbon dioxide by wet chemical methods or by "ashing" at high temperatures.

We investigated an alternative method of wet chemical pressure digestion with concentrated nitric-sulfuric in tightly closed polyethylene bottles (Adrian 1971). The pressure digestion appears to dissolve the fish but residual brown color in the solution indicated that not all organic compounds were oxidized to carbon dioxide. This conclusion was confirmed by adding potassium permanganate.

A combination of wet and dry ashing was found to give the best results in terms of completeness of digestion and recovery of spiked samples. To one gram of material in a 15 ml Vitreosil crucible is added 1 ml of concentrated reagent grade nitric acid. The sample is then heated on a hot plate until evolution of brown NO_2 gas ceases. This procedure is repeated 3 times.

Predigestion with nitric acid serves to oxidize the bulk of the easily oxidizable organic material and leaves a thin crust of material spread evenly on the bottom and sides of the crucible. The crucible is heated at 500°C for 24 hrs and the remaining white ash is dissolved in 2N HCl and analyzed directly by flame atomic absorption spectrometry. HCl is used as the solvent because of the superior complexing ability of the chloride anion.

D. Analytical

1. Atomic Absorption

The heavy metal cation concentration in effluent samples and fish was determined with a Varian Techtron AA-5 atomic absorption spectrophotometer.

Most of the analyses were performed by the conventional flame method. Some samples were analyzed with a Perkin-Elmer Heated Graphite Analyzer accessory which improved sensitivity and precision.

Effluent samples were prepared for AA analyses by filtering through a 0.45 micron Millipore filter. The filtrate was acidified to pH 2 with 2M hydrochloric acid. Initially, the filter and suspended particles from the effluent were reflux digested 3 times to dryness with concentrated nitric acid. The digested filter and residue were then dissolved in 2M HCl.

The reflux digestion method did not appear to oxidize thoroughly all organics since a brown color persisted in the digestant. Ashing the filter and particulate matter at 550° C for 16 -- 20 hrs produced a clear white ash which would completely dissolve in 2M HCl.

2. Chromatography

a. Thin layer chromatography

Thin layer chromatography (TLC) was used to separate and clean up fractions from the concentrated organic extracts. The samples were spotted or streaked on TLC plates (Brinkman) pre-coated with silica gel or alumina. Various solvents and solvent mixtures were investigated. Chloroform: methanol (99:1) and chloroform:hexane (1:1) appeared to produce the best resolution. TLC spots were scraped from glass plates and taken up into a Pasteur pipette plugged with glass wool.

Column chromatography was performed on some samples to clean up the extracts for subsequent analyses. A glass column 5 mm OD x 20 cm long filled with Davidson Code 950 Silica Gel G was used as the stationary support. The sample was sequentially eluted from the column with 25 ml of hexane, methylene chloride, chloroform and methanol.

Gas liquid chromatography (GLC) was performed on F & M Model 810 dual hydrogen flame, F & M Model 700 thermal conductivity, and Hewlett Packard 5755B dual hydrogen flame and electron capture detector gas chromatographs. Non-polar OV-1, UCW-98, SE-30 type supports gave good resolution. A combination of stainless steel 1/8" x 10' 5% OV-17 followed by stainless steel 1/8" x 10' 5% OV-1 coated on high performance Chromosorb-W yielded the best separations and lowest bleed off of liquid phase.

Typical operating conditions were: temp., oven, 100° C programmed to 250° C at 10°/min; injection port, 200° C; detector block, 285° C; Helium carrier gas, 60 c/min; hydrogen, 50 cc/min; compressed air, 400 cc/min; and recorder speed, .25 in/min.

Suspected toxic fractions were chromatographed to obtain a "finger print" for comparison with known standard compounds and to obtain good resolution of peaks. Samples which could be resolved into individual component peaks were marked for subsequent analyses by a combination LKB-9000 chromatograph - mass spectrometer (Waller 1968).

Most samples could not be resolved into individual compounds peaks but appeared to be very complex mixtures of similar isomers which could not be separated under the conditions of operation.

Suspected toxic fractions that could be resolved were characterized by mass spectral scans of the compounds as they eluted from the GC. The mass spectral scans were hand-measured and the spectra normalized by subtracting "background" scans, calculating % sigma (the percentage of any measureable m/e to the sum of all peaks), relative intensity (the percentage of any m/e to the most intense m/e in the scan), and then plotted by a Calcomp X-Y plotter.

RESULTS AND DISCUSSION

The first phase of this investigation was designed to develop a procedure for isolating a toxic fraction from the oil refinery effluents. Initially, several different procedures were used to extract fractions for toxicity tests. The extracted fraction and the effluent after extraction were bioassayed with daphnids. Some procedures were discontinued because of interferences, negative, or inconclusive results.

The most significant results were obtained with a flash-evaporation procedure. Previous experience with refinery effluents had shown that the acute effects to daphnids could be reduced simply by allowing the samples to set open in the laboratory. The observed reduction in toxicity could have been caused by loss of volatile toxins, precipitation of toxins, or bacterial decomposition. Aeration of the effluent quickly reduced the toxicity of the effluent (Table III) which indicated either that volatile toxins were evaporated or that bacterial decomposition was accelerated.

Table III

Microbioassay
10-29-70

ETU 60.10 October sample used

To determine if length of time sample is exposed to air affects the toxicity.

First sample collected 10-19-70 from unopened 5 gal container. Micro bioassay from that sample on same day: <5 min.

	Hours	Minutes
1. 0 minute on magnetic stirrer (9:05)	23	55
2. 7 minutes on magnetic stirrer (9:15)	23	45
3. 11 minutes on magnetic stirrer (9:33)	23	27

Above samples taken from sample collected 10-19-70 and tested 10-29-70. All samples alive at 5 PM, but dead by 8 AM.

Table 3. Continued

New samples collected and tested 10-29-70.

	Hours	Minutes
1. 0 minutes on magnetic stirrer		10
2. 10 minutes on magnetic stirrer		10
3. 15 minutes on magnetic stirrer		11
4. 30 minutes on magnetic stirrer		14
5. 45 minutes on magnetic stirrer		27
6. 1 hour on magnetic stirrer		35
7. 2 hours on magnetic stirrer	1	31

A rotating thin film flash evaporator was purchased to determine if volatile toxins could be stripped and collected from the effluents. The toxicity of the flash evaporation volatile (FEV) fraction to daphnids was much greater than the original effluent sample or the non-volatile residuum after flash evaporation (Table III). These results indicated that a major portion of the acutely toxic compounds in refinery effluents were volatile and could be stripped from the effluent.

The other procedures used to isolate toxic compounds did not achieve such significant results as the flash-evaporation but were informative in determining the general nature of toxins in refinery effluents.

Organic compounds in acutely toxic effluents and in non-toxic effluents were investigated by extracting the effluents with hexane, toluene, and methylene chloride to remove three different fractions of organic compounds. The toxicity of the extracted fractions was used as a criterion to determine whether the solvent extraction had isolated the toxic compounds. Since the solvent fractions contained only small quantities of organic compounds the regular fish bioassay could not be

Table III

COMPARISON OF NON-VOLATILE AND VOLATILE FRACTIONS

	#4 oxid Pond	Outfall		SI	60.10			Effluent	
	BQB	DPQ-W	DPF	ETE	ETU	LNK	NDD	DPQ-E	UWU
<u>Jan. 71</u>									
1-11-71									
pH									
original	7.5	7.1	7.4	7.9	8.4	9.0	9.5	8.9	7.0
vol.	8.2	7.6		8.4	8.4	8.4	7.9	7.0	7.7
non-vol.	7.7			7.0				8.4	7.7
Microbioassay									
original	>4- 0- 0	2- 5-40	<2- 0- 0	0- 0- 6	0- 0-55	0- 0- 3	0- 0-35	0-22-20	1-18-20
vol.	0- 0- 4	0-<20-0		0- 0- 2	0- 0- 3		0-<20-0	2- 2- 0	0- 0-20
non-vol.	>4- 0- 0	>4- 0- 0		0-<23-0			>4- 0- 0	2- 2- 0	>4- 0- 0
<u>Feb. 71</u>									
A									
pH									
original	7.7	7.2	7.0	7.8	8.2	6.1	7.7	8.0	6.8
vol.	8.3	8.2	8.4	8.3	8.5	8.4	8.0	8.2	8.3
non-vol.		7.9	7.5	7.9	7.5	6.8	8.2	7.0	7.2
Microbioassay									
original	0-23-15	0- 7-40	0-<21-0	0- 0-10	0- 0-40	1-19- 0	0- 6-45	0- 1-30	0-22-45
vol.	0- 0- 3	0- 0-12	0-0-(1-2)	0- 0- 3	0- 0- 3	0- 0-20	0- 0- 4	0- 0- 4	0- 0-13
non-vol.	1-18-45	2-19-46	1-17-30	0- 0- 7	0-<21-40	1-16-25	>4- 0- 0	>4- 0- 0	2- 0- 5
<u>March 71</u>									
C									
263E									
pH									
original	6.6	7.4	8.2	7.1	N	7.1	7.8	7.8	6.8
vol.		8.4	8.6	8.3	O	8.3	8.2	8.3	8.7
non-vol.	7.8	7.7	8.5	8.0	S	7.2	8.3	7.7	8.1
Microbioassay									
original	0- 2- 0	>4- 0- 0	1 sec.	1- 0- 0	A	0-18- 0	0- 1- 0	0- 1- 0	1-18-45
vol.	0- 0- 7	0- 0- 2	1 sec.	0- 0- 3	M	0- 0- 3	0- 0-15	0- 0- 2	0- 0- 1
non-vol.	2- 2-30	<1- 0- 0	50sec.	1- 1- 7	P	1-17-21	1-17-20	0- 0-30	1-18- 0
<u>April 71</u>									
A									
292E									
pH									
original	7.0	7.2	7.6	7.5	10.2	7.2	7.3	8.5	6.5
vol.	9.1	8.3	8.8	8.8	9.9	9.6	8.9	8.3	9.4
non-vol.	8.0	9.2	8.9	7.8	9.8	9.0	8.9	8.7	7.8
Microbioassay									
original	>4- 0- 0	<1-20-45	>4- 0- 0	0- 0-15	0- 0-10	>4- 0- 0	<1- 0- 0	1- 3-15	<1-21- 0
vol.	0- 2- 4	0- 0-44	0- 0- 4	0- 0- 6	0- 0- 1	0- 0-19	0- 0-19	0- 0- 7	0- 3-22
non-vol.	>4- 0- 0	0- 1-54	1- 2-19	<0-21-15	<0-19-30	>4- 0- 0	<3-22-34	>4- 0- 0	<1-23- 0
<u>May 71</u>									
C									
323E									
pH									
original	7.3	7.0	8.1	7.1	8.5	7.5	8.3	8.4	8.
vol.	8.2	8.0	8.2	8.6	8.6	7.3	8.5	8.4	8.3
non-vol.	8.1	8.5	7.6	7.8	8.4	8.3	8.2	8.3	8.4
Microbioassay									
original	>4- 0- 0	>4- 0- 0	>4- 0- 0	<1- 4-58	0- 0- 3	>4- 0- 0	0- 0- 6	0-20-30	0- 0- 6
vol.	0- 0- 5	0- 0-33	0- 3-21	<0- 0- 1	0- 0-15	<0-19-14	0- 0- 1	0- 0-10	0- 0-44
non-vol.	3- 1-20	>4- 0- 0	>4- 0- 0	1- 3-16		>4- 0- 0	0- 1- 5	1- 7-22	1-18-20

50-75 ml. condensed from 500 ml. of sample with flash evaporator to form volatile fraction.

Table III
(Continued)

COMPARISON OF NON-VOLATILE AND VOLATILE FRACTIONS

	BQB	DPQ-E	DPQ-W	DPF	ETE	ETU	LNK	NDD	UWU
<u>June 71</u>									
pH									
original	7.8	7.0	7.1	7.2	7.0	8.3	6.9	7.7	7.2
vol.	8.3	8.1	7.9	8.2	8.1	8.5	7.5	8.1	8.3
non-vol.	7.9	8.2	8.2	8.0	7.2	8.3	7.1	8.3	8.1
Microbioassay									
original	4- 0- 0	(3-4)-0-0	(3-4)-0-0	4- 0- 0	0- 0-17	0- 0-16	4- 0- 0	1- 3- 0	3- 0-28
vol.	0- 0- 4	0- 1-30	(3-4)-0-0	0- 0- 3	0- 0- 3	0- 0-1.5	4- 0- 0	0- 0- 5	0- 0-12
non-vol.	4- 0- 0	(3-4)-0-0	4- 0- 0	0-21-14	0-21-14	0- 0-50	4- 0- 0	0- 3-35	(3-4)-0-0
<u>July 71</u>									
pH									
original	N	7.5	7.6	7.2	7.0	8.6	N	N	7.0
vol.	O	8.4	7.4	8.2	8.4	8.5	O	O	8.5
non-vol.		7.2	8.1	8.3	6.3	8.1			8.1
S									
A									
original	M	3- 9-30	4- 0- 0	0- 2- 0	1- 1-19	0- 0- 4	M	M	0-22-39
vol.	P	0- 0-33	0-17-43	0- 0- 3	0- 0-10	0- 0- 1	P	P	0- 0-10
non-vol.	L	2-17-43	4- 0- 0	4- 0- 0	0-21-17	0- 0-25	L	L	(3-5)-0-0
E									
<u>Aug. 71</u>									
pH									
original	8.3	7.8	7.0	7.2	7.0	7.3	6.6	7.4	7.1
vol.	8.5	8.5	8.2	7.6	8.3	8.2	7.9	8.4	8.1
non-vol.	8.1	7.0	8.1	8.3	7.4	7.8	6.7	8.4	8.1
Microbioassay									
original	4- 0- 0	2-18-40	4- 0- 0	0- 1-25	0- 0-29	0- 6-12	4- 0- 0	4- 0- 0	2-18-40
vol.	4- 0- 0	0- 0-11	0- 0-27	0- 0-42	0- 0- 3	0- 0- 2	0- 2-30	0- 1-10	0- 0- 3
non-vol.	4- 0- 0	0-20-56	4- 0- 0	0-2-42	0-20-30	0- 2-42	4- 0- 0	3-23-40	4- 0- 0

Table III
(Continued)

COMPARISON OF NON-VOLATILE AND VOLATILE FRACTIONS

<u>March 71</u>	LND
pH	
original	7.7
vol.	8.6
non-vol.	7.6
Microbioassay	
original	0- 0- 7
vol.	0- 0- 1
non-vol.	0- 1-10

used to detect the toxicity of the extract, and used a microbioassay with Daphnia sp. as the test organism. The Daphnia bioassay can be conducted in 50 ml of water requiring only a few mg of organics to obtain concentrations of 50 to 100 mg/l.

Extracted effluents were generally more toxic than the original effluent, apparently because of solvent residues in the effluents. This was confirmed by extracting dechlorinated tap water, which was non-toxic to Daphnia, with the solvents and exposing Daphnia to the extracted tap water. The Daphnia were killed in a short period of time. Apparently the water retained enough of the solvent to be toxic. The solvent could not be removed by aerating, stirring or other simple physical methods.

Microbioassay
10-23-70

To determine if excess CH_2Cl_2 in water phase of CH_2Cl_2 extract procedure could be removed by the flash evaporator thus permitting a valid microbioassay for water phase.

Water phase + excess CH_2Cl_2

↓
flash evaporator

light suction (2 hr)

60° C water bath

ice bath for solvent flask

↙ volatiles + CH_2Cl_2 excess

↘ water phase

microbioassay

BQB #3 oil pond
UWU

<1 minute
5 seconds

To determine if stirring on a magnetic stirrer will reduce excess hexane from water phase of hexane extract procedure thus permitting a valid microbioassay for the water phase. Three hr stirring per sample of 1000 ml.

BQB #3 oil pond
ETU 60.10

<50 minutes
1 minute

The quantity of methylene chloride extractables was greater than the hexane extract. Non-polar hydrocarbons were extracted with hexane and the concentration was a semi-quantitative measure of the oil content of the water. Some hydrocarbons plus more polar organic compounds were extracted with the methylene chloride. Toluene extracts were discontinued after two months since they were more difficult to evaporate at room temperature and overlapped both hexane and methylene chloride in the types of compounds extracted.

The concentrated solvent extracts were dark brown to black in color, very viscous, and had an "asphaltic" odor. Attempts to redissolve the solvent extracts in dechlorinated tap water to perform bioassays were not very successful. The concentrated extracts could be dissolved in water only by dispersion with acetone.

Concentrations of 50 and 100 mg/l of the methylene chloride extracts were prepared by dissolving the extracts in acetone and mixing them with tap dechlorinated water. The aqueous solution of the extracts were then bioassayed with daphnids. The results of these tests were inconclusive in that there appeared to be no significant difference between the toxicity of the extract and the original effluent. In some cases where the extract was highly toxic, it was possible that some residual methylene chloride could have caused the toxicity. The value of this procedure for isolating toxins from refinery effluents could not be determined because of the difficulties encountered.

Effluent samples were passed through activated carbon columns filled with NuChar C-190 to determine if activated carbon would absorb toxic organics from the effluent. Activated carbon removes some but not all of the toxins. The activated carbon was subsequently extracted with chloroform and alcohol to remove adsorbed compounds for chromatographic

analyses. The carbon chloroform extract was quite complex and did not contain enough volatile compounds for gas chromatographic analyses. The resolution of individual peaks (compounds) was not sufficient to permit any further analyses of these extracts without additional clean-up. Some of the extracts were subjected to thin layer chromatography (TLC) and column chromatography (CC) to reduce the complexity of the mixtures. The TLC and CC fractions were then injected on the gas chromatograph to determine the number of compounds and complexity of the fractions. Resolution was still not good. Since the toxicity bioassays had indicated that the activated carbon adsorbed only some toxic substances, further analyses were not attempted on these fractions. Increased analytical effort was directed towards the demonstrably toxic flash evaporation fractions.

The compounds extracted from the refinery effluents by flash evaporation were significantly more toxic than any other fractions. The rotating thin film flash evaporator continually exposes a large surface area for volatilization of steam and organic compounds. The procedure appears to be much more efficient for removing toxic compounds than steam distillation at atmospheric pressure. In 1969 - 1970 steam distillation was used for extracting compounds from the effluents for identification purposes. A few bioassays were performed on the steam-distilled effluent and the toxicity did not appear to be reduced. The compounds identified in the steam distillation were a homologous series of normal aliphatic hydrocarbons from undecane through octadecane.

The flash evaporation procedure in almost all cases (90%) removed a volatile fraction which was much more toxic than the original effluent (Figs. 2-10) or the residual non-volatile compounds left in the effluent sample after flash evaporation. Most of the toxins were removed from the effluent by 10 to 20% evaporation (Table IV).

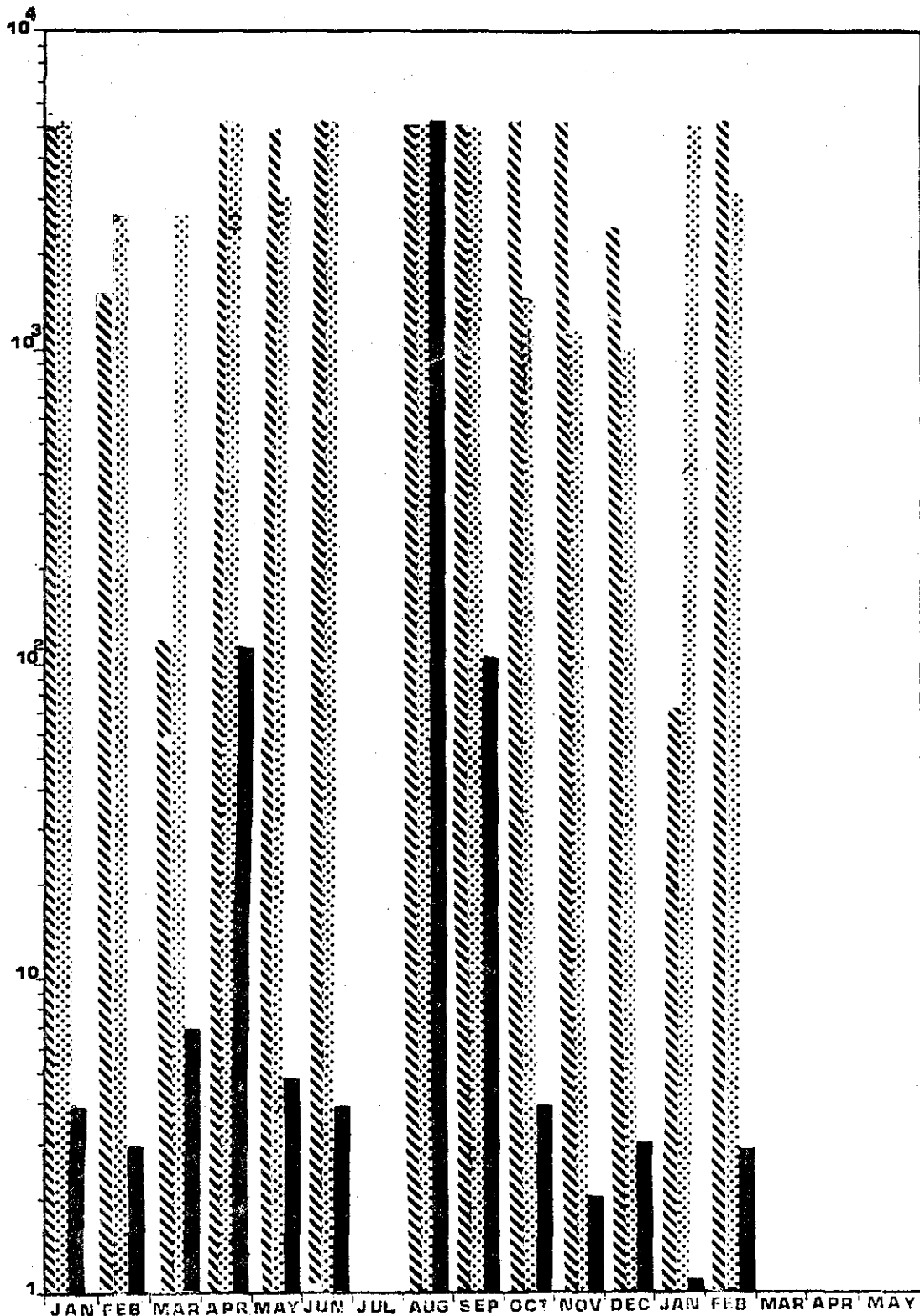


Fig. 2. Survival time (minutes) of Daphnids exposed to BQB final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

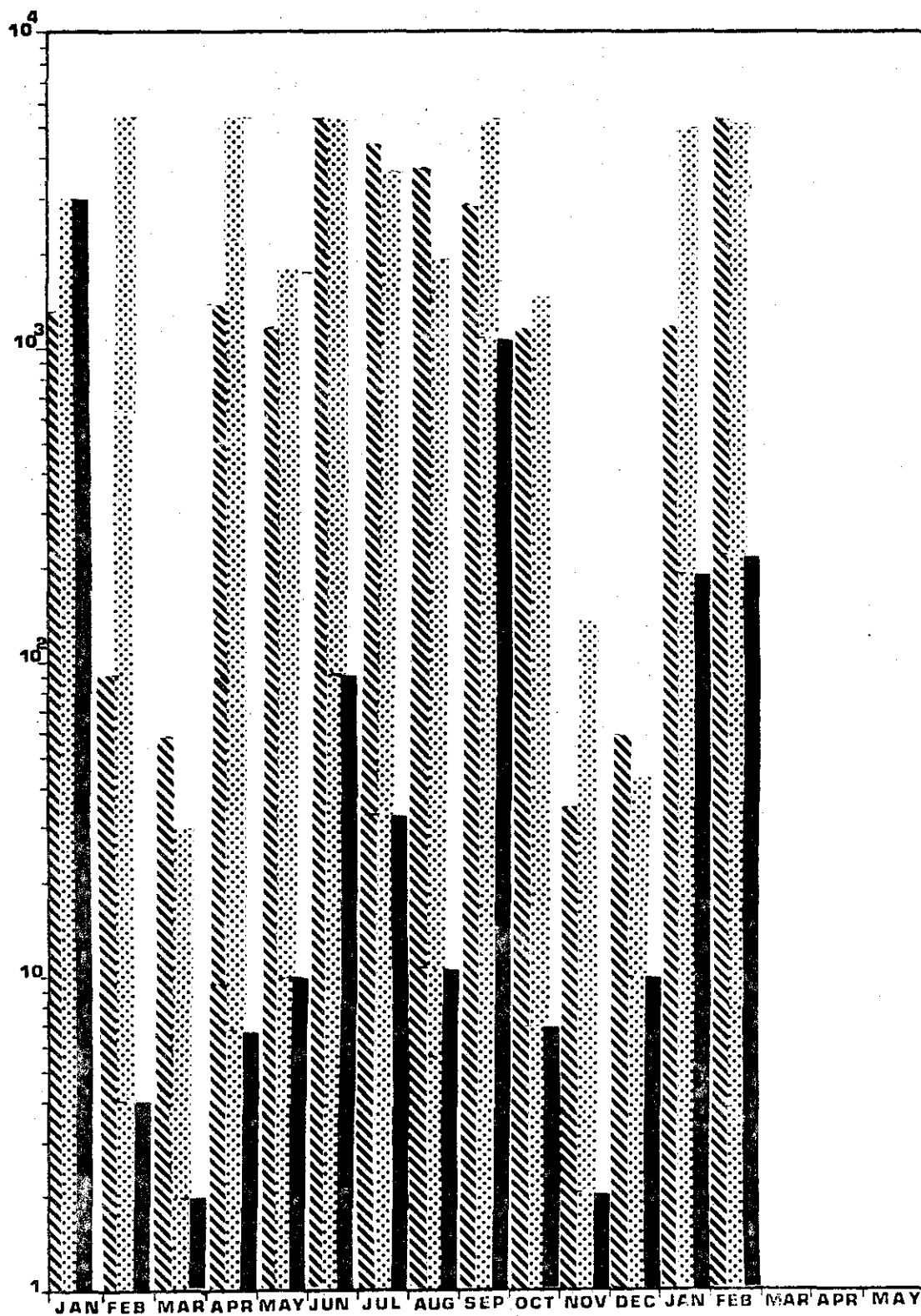


Fig. 3. Survival time (minutes) of Daphnids exposed to DPQ-E final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

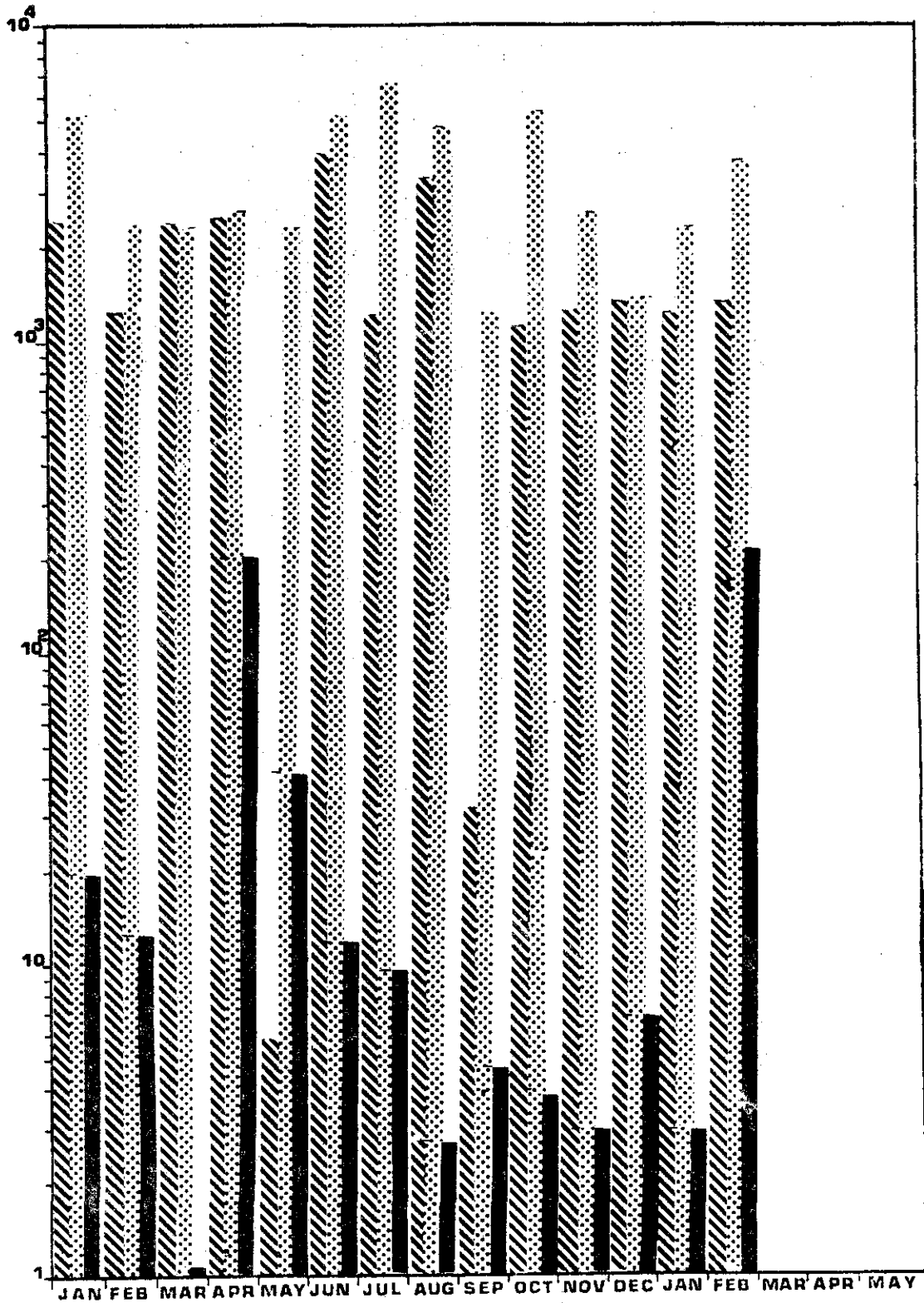


Fig. 4. Survival time (minutes) of Daphnids exposed to UWU final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

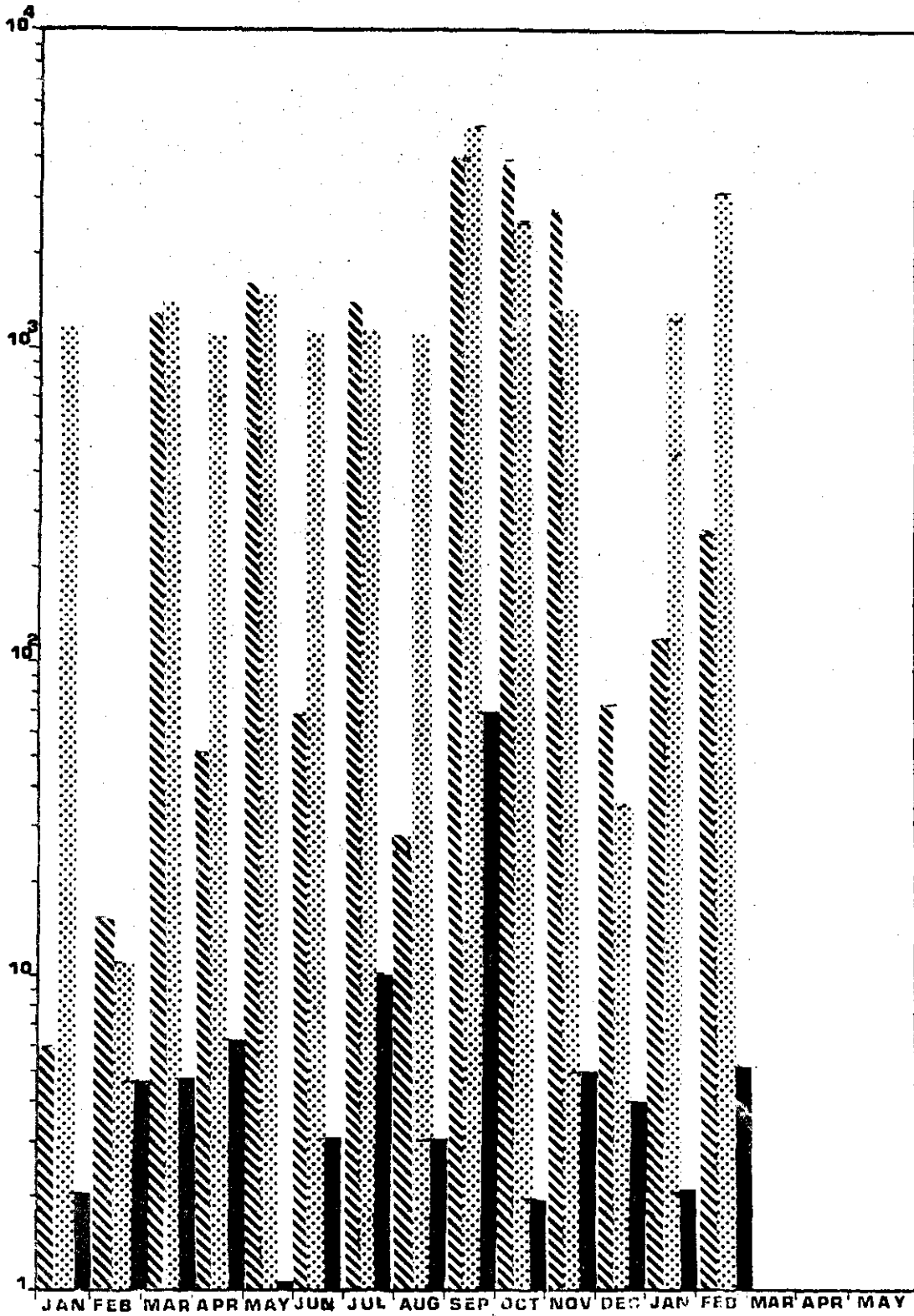


Fig. 5. Survival time (minutes) of Daphnids exposed to ETE final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

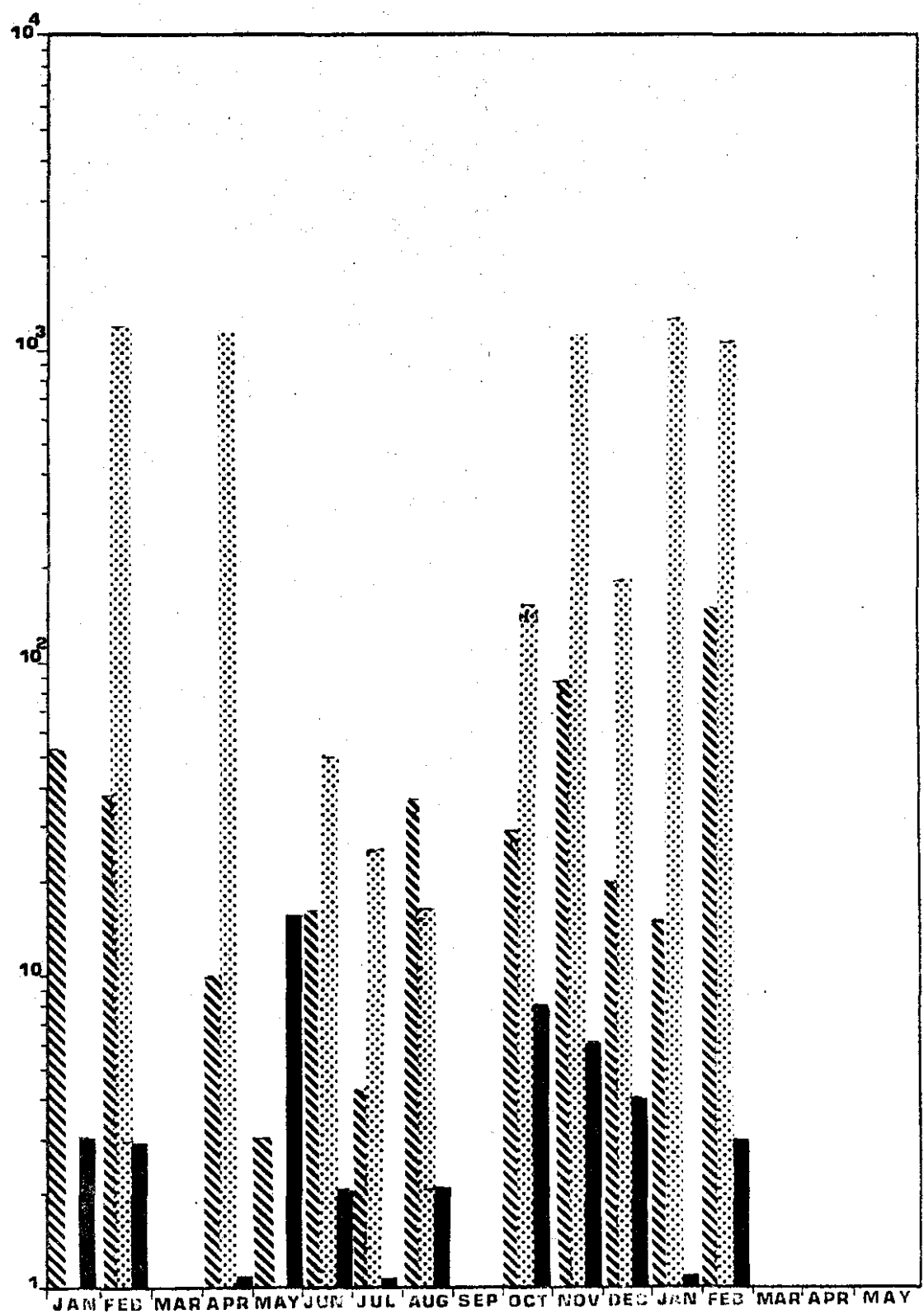


Fig. 6. Survival time (minutes) of Daphnids exposed to ETU final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

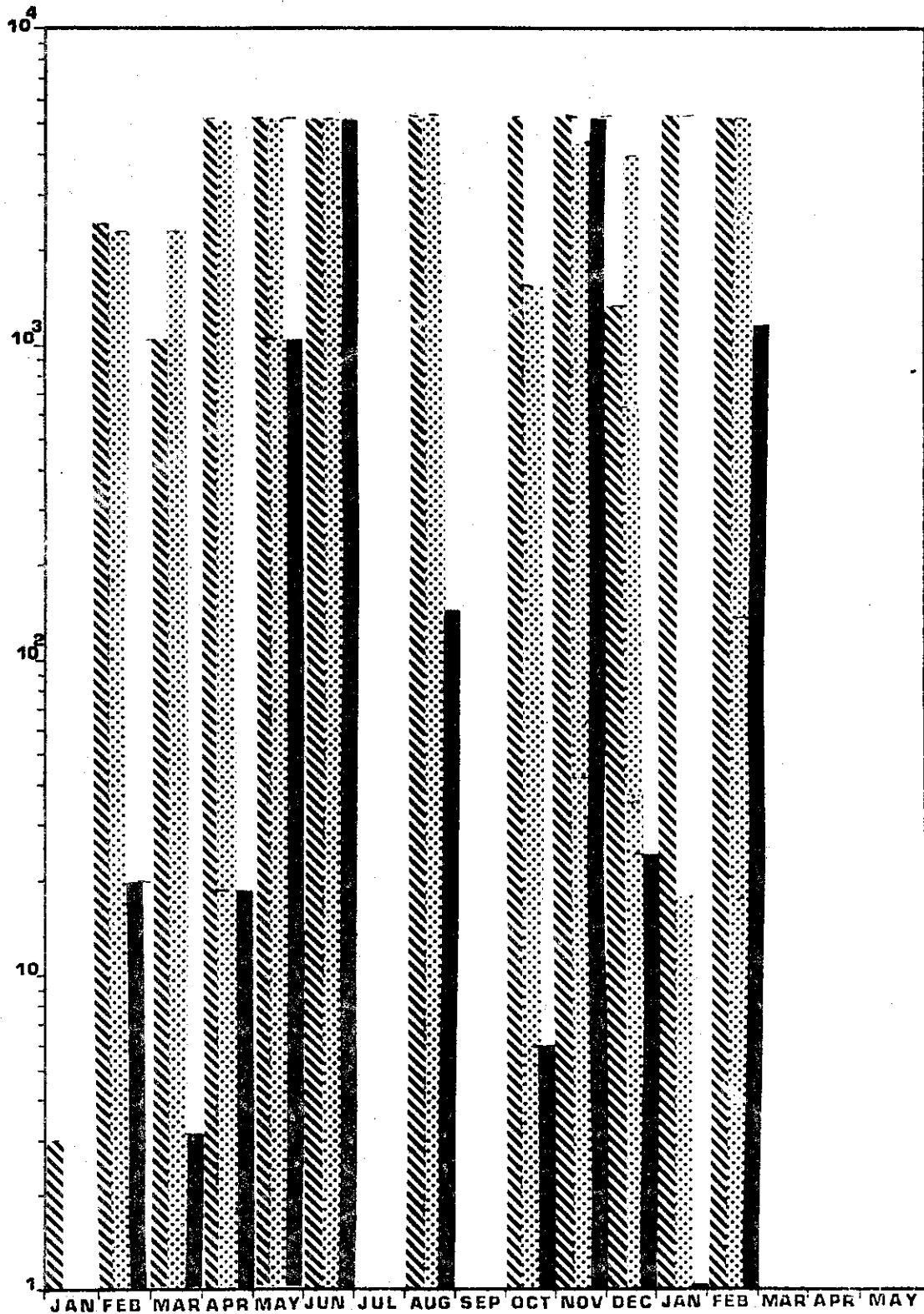


Fig. 7. Survival time (minutes) of Daphnids exposed to LNX final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

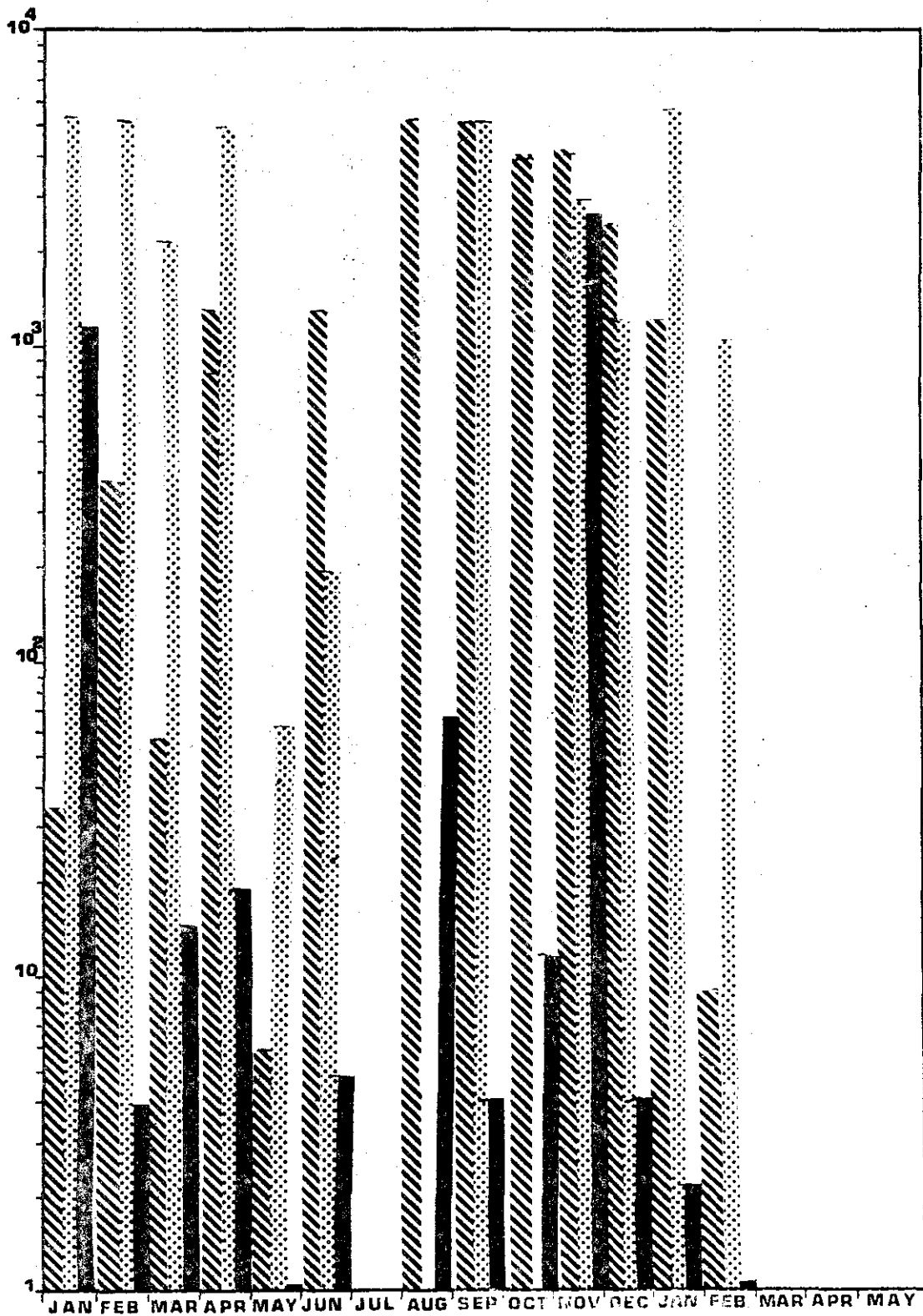


Fig. 8. Survival time (minutes) of Daphnids exposed to NDD final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

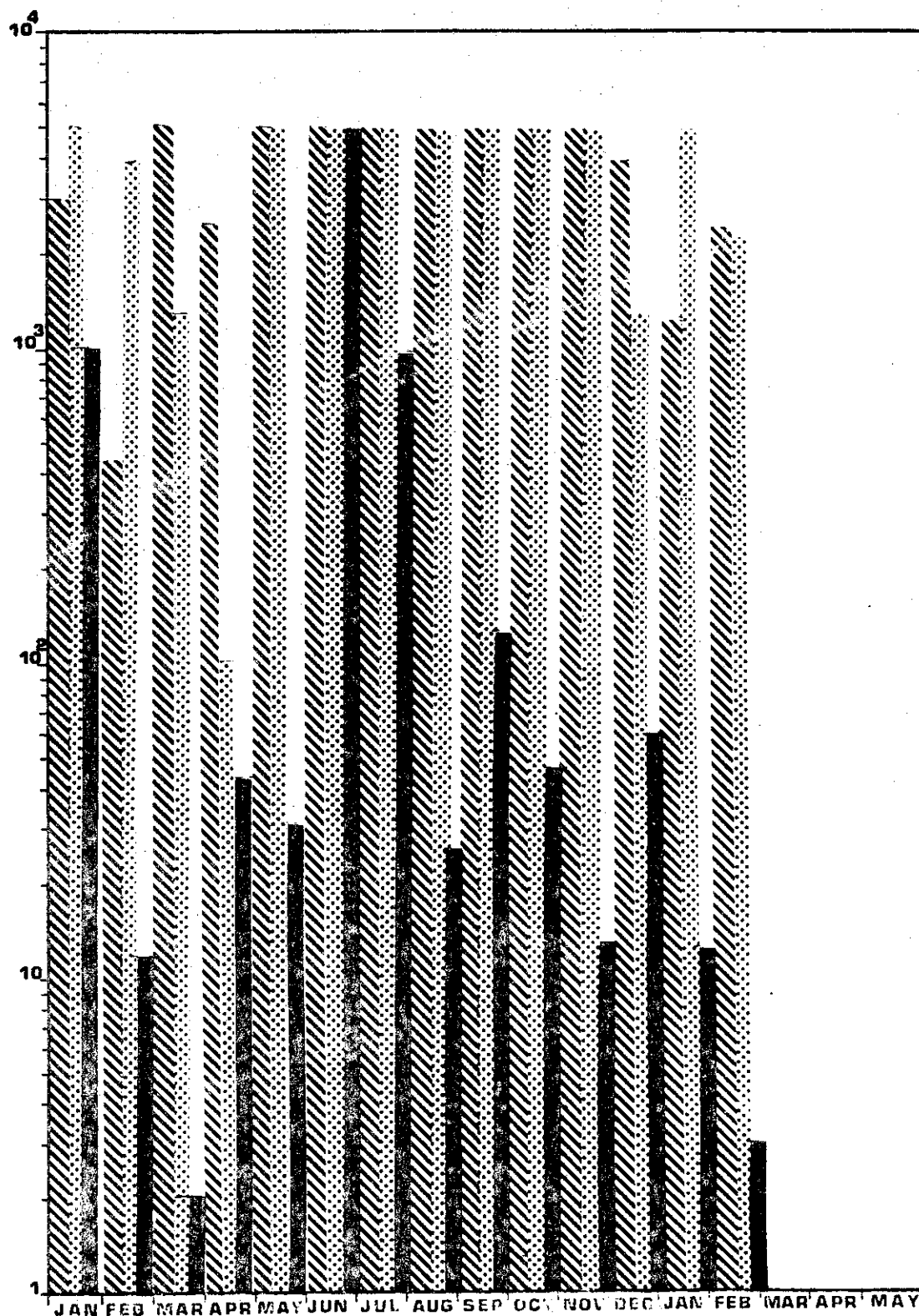


Fig. 9. Survival time (minutes) of Daphnids exposed to DPQ-W final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

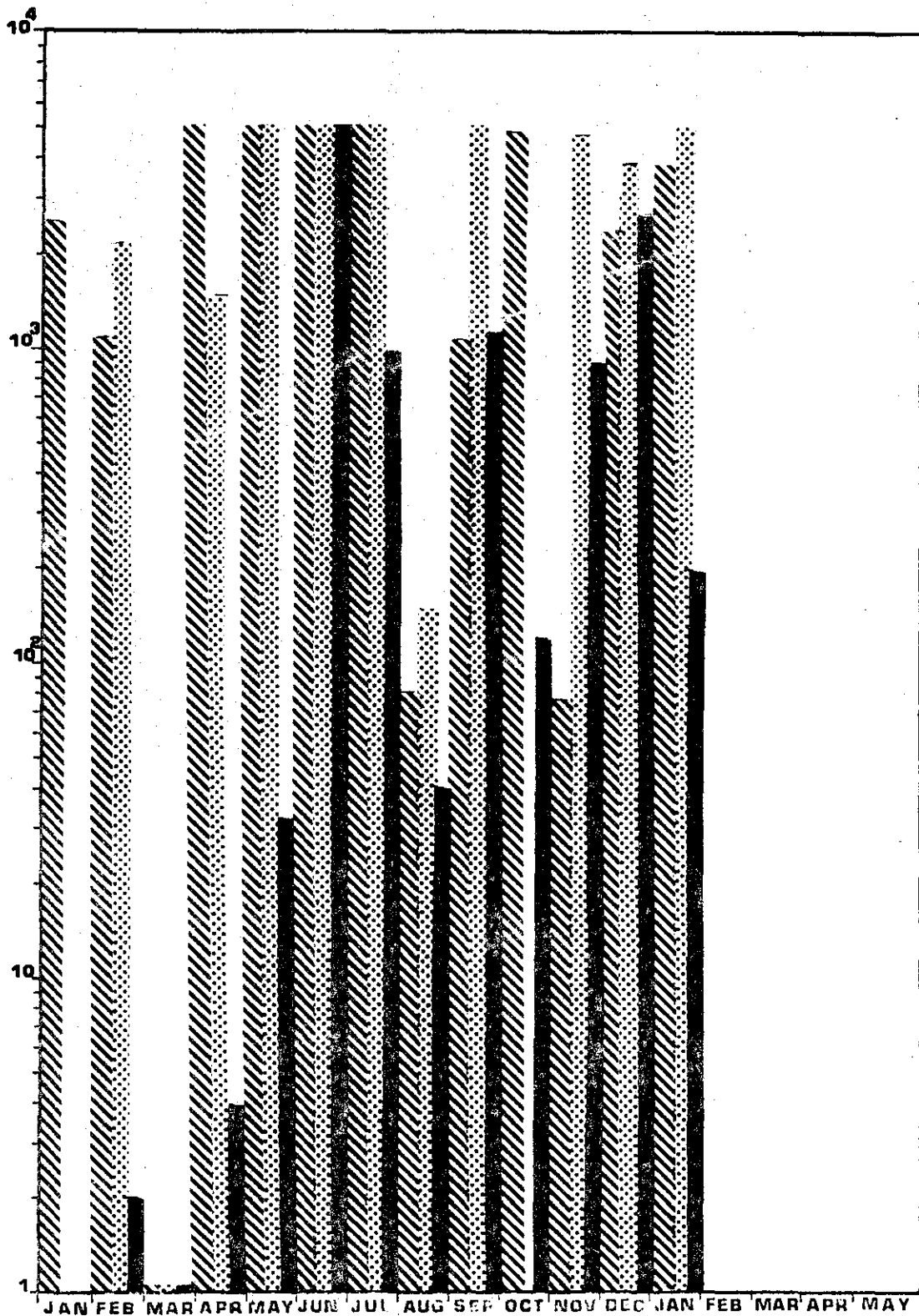


Fig. 10. Survival time (minutes) of Daphnids exposed to DPF final effluent (diagonal), non-volatile residuum (stippled), and flash evaporation extract (solid).

TABLE IV
 TEST TO DETERMINE OPTIMUM
 REMOVAL OF TOXINS BY FLASH EVAPORATION

Volatile Flash Evaporation Fraction			Non-Volatile Residual After Flash Evaporation		
Percent	pH	Daphnid Bioassay Survival Time Days-Hours-Min.	Percent	pH	Daphnid Bioassay Survival Time Days-Hours-Min.
10	8.5	0-0-1.5	90	8.1	0-1-55
20	8.2	0-0-2.5	80	8.0	>4-0-0
30	8.3	0-0-2.5	70	7.8	*>0-8-0 <0-22-0
40	8.3	0-0-3.5	60	7.3	*>0-8-0 <0-22-0
50	8.5	0-0-4.0	50	6.8	*>0-8-0 <0-22-0

*Daphnids survived longer than 8 hours but less than 22 hours.

An oil refinery effluent which had been treated by an activated sludge system was evaporated with a Buchler Model FE-2C rotating-film continuous-flow laboratory evaporator. Ten liters of the effluent feed water was evaporated to a final volume of 30 ml. Nineteen 500 ml samples of the product condensate water and eighteen 30 ml samples of the brine concentrate were collected during the run. The 30 ml samples of brine concentrate were withdrawn after each 500 ml fraction of product water was produced. The volume of the brine slurry in the hot evaporating flask was not maintained constant, so that the relative volumes of the 30 ml samples and the concentrations of dissolved solids fluctuated (Table V).

Acute toxicity bioassays were performed on every fifth sample of the product water and the brine with Daphnia magna (Fig.11). The first

Table V. Chemical Analyses of Product and Brine Water
From Evaporation of Oil Refinery Effluent

	Brine % Conc. from Original	Daphnid Bio-assay	Cl mg/l	F mg/l	Na mg/l	Ca mg/l	K mg/l	Mg mg/l
1st 500 ml FEV	2/11	0-22-25						
1st Brine Sample	2/11 50%		115	0	700	50	13	25
2nd 500 ml FEV	2/12							
2nd Brine Sample	2/12 33 $\frac{1}{3}$ %		220	0	1100	130	25	30
3rd 500 ml FEV	2/12							
3rd Brine Sample	2/12 25%		235	0	1500	180	25	50
4th 500 ml FEV	2/14	1-21-25						
4th Brine Sample	2/14 16.6%	<1-0-0	335	0	2600	330	65	70
5th 500 ml FEV	2/12							
5th Brine Sample	2/12 20%		300	0	2000	230	48	60
6th 500 ml FEV	2/14							
6th Brine Sample	2/14 12.5%		500	15	4200	620	140	115
7th 500 ml FEV	2/14							
7th Brine Sample	2/14 14.2%		355	0	2800	360	70	80
8th 500 ml FEV								
8th Brine Sample	2/14 6:15P 10.0%		510	11	4700	700	145	120
9th 500 ml FEV								
9th Brine Sample	2/14 4:30P 11.1%		500	11	4100	650	135	125
10th 500 ml FEV								
10th Brine Sample	8.3%		750	14.8	6000	820	200	165
11th 500 ml FEV								
11th Brine Sample	2/14 7:45P 9.9%	0-1-6	505	10.5	3600	530	100	100
12th 500 ml FEV	2/15							
12th Brine Sample	2/15 7.7%		503	11.8	3400	480	95	100
13th 500 ml FEV	2/15							
13th Brine Sample	2/15 7.14%		500	13.0	4000	1750	125	215
14th 500 ml FEV	2/15							
14th Brine Sample	2/15 6.6%		460	0	2900	440	75	95

Table v (Continued)

	Brine % Conc. from Original	Daphnid Bio-assay	Cl mg/l	F mg/l	Na mg/l	Ca mg/l	K mg/l	Mg mg/l
15th 500 ml FEV								
15th Brine Sample	2/15 3:30P 6.25%	0-0-27	515	12	3500	560	100	100
16th 500 ml FEV								
16th Brine Sample	2/15 5:00P 5.88%		1170	13	7700	1170	325	155
17th 500 ml FEV								
17th Brine Sample	5.5%		729	16	5000	960	170	160
18th 500 ml FEV								
18th Brine Sample	2/15 7:15P 5.25%		730	11	5700	970	195	175
19th 500 ml FEV								
19th Brine Sample	2/15 8:45P 5%	0-0-13	1200	16	9400	2300	380	310

Table V (Continued)
 SPECIFIC ION PROBE ANALYSES OF
 BRINE SAMPLES FROM CONTINUOUS
 FLASH-EVAPORATION OF REFINERY EFFLUENT SAMPLE

DPQ-East January 72		Cl ⁻ ppm	F ⁻
1. Brine	50 % conc.	115	0
2. Brine	33.3% conc.	220	0
3. Brine	25 % conc.	235	0
4. Brine	20 % conc.	300	0
5. Brine	16.6% conc.	335	0
6. Brine	14.2% conc.	355	0
7. Brine	conc.	500	15
8. Brine	11.1% conc.	500	11
9. Brine	10 % conc.	510	11
10. Brine	9.9% conc.	505	10.5
11. Brine	8.3% conc.	750	14.8
12. Brine	conc.	503	11.8
13. Brine	conc.	500	13
14. Brine	conc.	460	0
15. Brine	conc.	515	12
16. Brine	5.88% conc.	1170	13
17. Brine	6.25% conc.	729	16
18. Brine	conc.	730	11
19. Brine	conc.	1200	16

NaCl as standard solution

100 ppm = 20

250 ppm = 48

400 ppm = 73

500 ppm = 88

NaF as standard solution

1 ppm F⁻ = 20

2 ppm F⁻ = 39.5

5 ppm F⁻ = 95

10 ppm F⁻ = 190

20 ppm F⁻ = 360

All the brine samples F⁻ were less than 1 ppm.

FORM SEMI-LOGARITHMIC 46 5490
11 x 14 3 CIRCLES TO DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

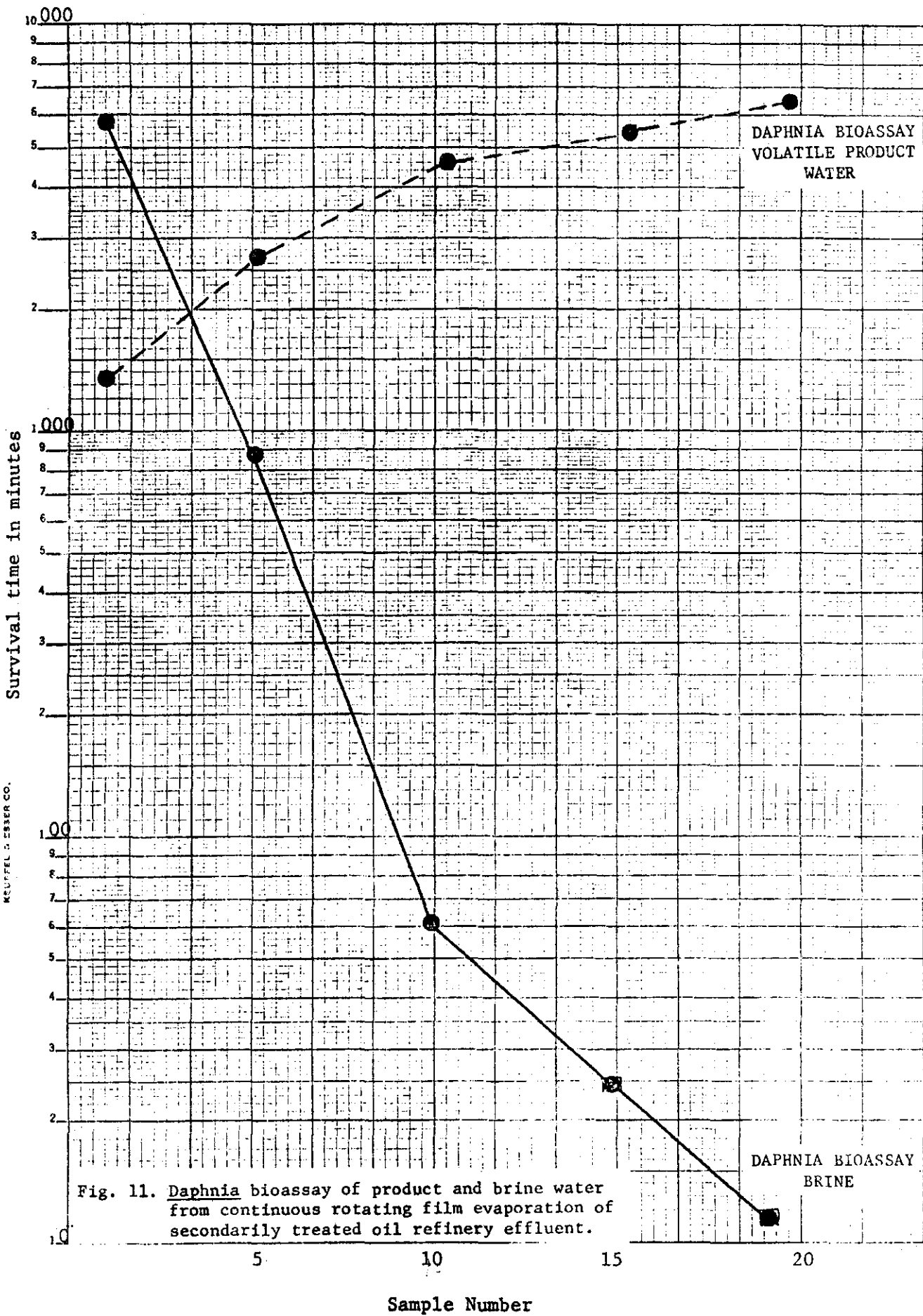


Fig. 11. *Daphnia* bioassay of product and brine water from continuous rotating film evaporation of secondarily treated oil refinery effluent.

volatile samples were more toxic than the brine samples; however, all of the brine samples after sample 5 were more toxic than the volatile samples. It appears that at approximately 75% boil-down most of the volatile toxins have been removed with the product water. The non-volatile residual toxins continue to increase and probably approach an asymptotic value. The brine slurry develops a dark brown color, which may be caused by non-volatile organics. We have not yet analyzed the brine slurries for total carbon or toxic cations such as copper, zinc, nickel, chromium, but this will be investigated.

The glass evaporative cell developed considerable scale during the boil-down, which might have been due to carbonates since the feed water was not degasified. We will decrease pH to 4 and strip with steam to prevent carbonates from entering the system and to strip sulfides and ammonia from the effluent feed water.

The pH of the flash evaporation volatile fraction (FEV) was generally higher than the original effluent (generally less than 8.5). Many of the refinery effluents contain ammonia, which may be vaporized from the effluent and collected in the FEV fraction. We have qualitatively checked for ammonia with red litmus paper, but have not found any ammonia in the FEV fraction. Most of the FEV fractions have been toxic in less than two hours and many were toxic in 20 minutes or less. The concentration of ammonia would have to be quite high to cause such rapid lethal effects and should be quite easily detected by litmus paper tests.

Extractions of an FEV fraction were made from receiving stream waters (Table VI) including Stillwater Creek below a municipal activated sludge waste treatment facility and the Cimarron River. The FEV fraction from the Cimarron River was slightly toxic (<29 hours), however, the remaining non-volatile fraction was toxic in 20 minutes compared to

Table VI

SPECIAL SAMPLES

	DPQ West unit traps H ₂ O			BQB #3 Oil Pond		Still- water Creek 4-9-71	Cim ² - ron River 4-9-71	DPF		DPF		Tap Water
	CCD	TCD	Light oil	pH 12	pH 4			F Municipal Effluent	D Cat Cracker	#1 Crude Unit De- Salter to Sewer	#2	
pH												
original	7.63	7.2	7.3	9.0	9.0	7.8	8.4	7.7	6.3	9.3	9.0	7.9
volatile	7.6	8.1	8.8	12.1	7.9	8.6	6.4	8.8	8.6	10.4	10.1	7.6
non-volatile	9.2	9.1	9.1	10.0	6.6	9.2	8.9	9.4	6.1	8.6	8.2	9.6
Microbioassay												
original	<1-0-0	0-2-14	1-5-44	0-0-27	0-0-27	2-4-20	0-0-50	>4-0-0	0-2-0	0-0-4	0-0-21	<0-18-40
volatile	<2-0-0	0-1-48	0-6-0	5 sec	<0-19-32	<0-20-0	<0-20-0	0-0-19	<0-18-17	0-0-1	0-0-15	1-0-20
non-volatile	<1-0-0	1-2-22	2-1-47	40 sec	<0-19-32	>4-0-0	0-0-20	1-23-22	<0-18-17	0-1-28	0-1-0	<1-18-40

52 hours for the original creek sample.

Extraction of FEV fractions from oil refinery process effluents have been utilized to determine the contribution of process effluent toxic constituents to the final effluent. DPF chemical de-salter unit #1 effluent was very toxic, and as a result of this analysis the refinery is planning to specially pre-treat the process effluent from its chemical de-salter units prior to combining with other process effluents for final treatment. This should result in a major improvement in final effluent quality.

FEV fractions from two different refineries were quite similar (Figs. 12 & 13). Sample 2/71 ETE-SI was subsequently analyzed on the gas chromatograph - mass spectrometer GC-MS. The ten most intense m/e ion fragments of eleven gas chromatographic peaks from ETE-SI are summarized in Table VII and compared to standard phenolic compounds. The mass spectra of scan 2066-2 (Fig. 14) shows good correspondence with O-cresol (2-methyl phenol). Positive position location of the methyl group on the phenol would require extensive chromatographic analyses which does not appear to be justified since the difference in toxicity or ortho-, meta-, and para -isomers of cresol are negligible.

Mass spectrometer scans 2066-3 (Fig. 15), 2066-5 (Fig. 18), 2066-6 (Fig. 19), 2066-7 (Fig. 20), 2066-8 (Fig. 21), and 2066-9 (Fig. 22) appear to be either dimethyl phenols or ethyl phenols, molecular weight 122. Mass spectrometer scan 2066-11 (Fig. 23) appears to be either trimethyl phenol, methyl ethyl phenol or propyl phenol. Mass spectrometer scan 2066-4 (Fig. 17) has molecular weight (M^+) 151. The odd molecular weight might indicate an odd number of nitrogen atoms in the compound or possibly that the m/e 151 is not the parent peak but an ion fragment. A tentative identification of this compound cannot be made until additional information is available.

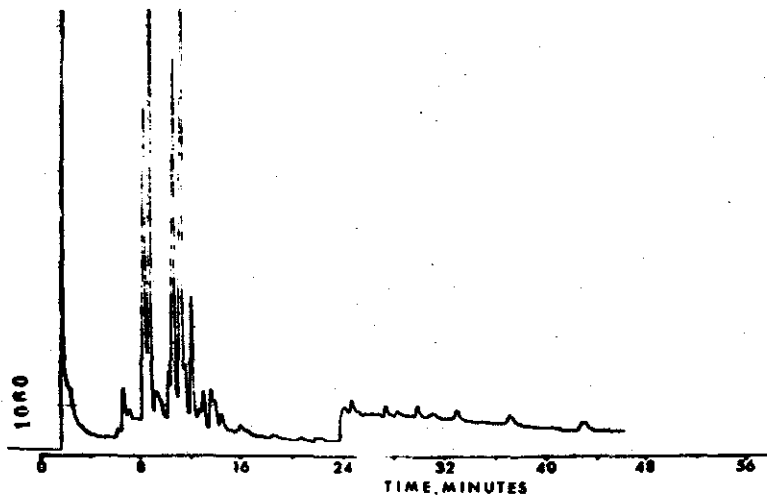


Fig. 12 Chromatograph of 2/71 ETE-SI - FEV fraction.

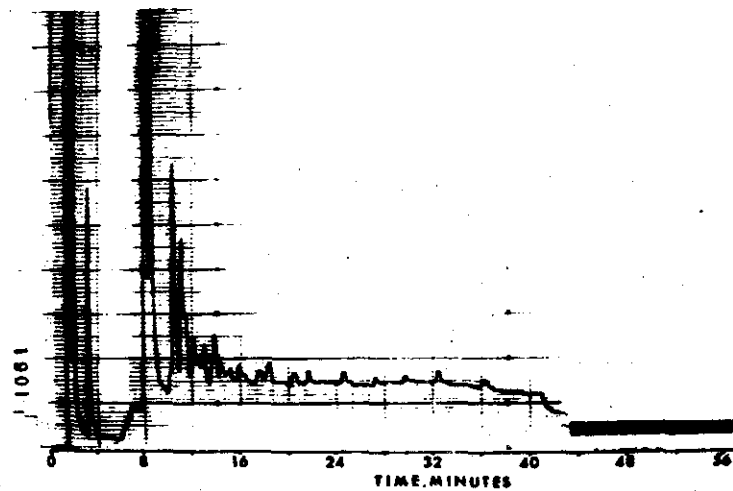


Fig. 13. Chromatograph of 1/71 LNX-234E - FEV fraction.

Table VII

Mass Spectra of ETE-SI-2/71 Flash Volatile - CH₂Cl₂ Extract
Ten Most Intense M/E Peaks

Scan No.	Base Peak	2	3	4	5	6	7	8	9	10	M ⁺
MS-2066-1	108	107	79	90	77	51	39	80	89	53	108
MS-2066-2	107	106	78	76	38	89	52	108	51	79	107
MS-2066-3	107	106	121	79	67	39	110	120	51	53	121
MS-2066-4	136	121	42	151	120	95	107	79	39	106	151
MS-2066-5	107	122	77	121	79	39	108	124	123	51	122
MS-2066-6	122	107	121	77	79	91	39	51	123	108	122
MS-2066-7	107	122	121	77	39	91	108	79	123	51	122
MS-2066-8	107	122	77	121	39	79	91	108	51	123	122
MS-2066-9	107	122	121	77	79	39	91	51	78	108	122
MS-2066-11	121	136	107	122	77	91	39	43	51	65	136
MS-2066-16	73	147	281	221	340	107	207	74	88	282	340
MS-2220-5	94	66	65	39	95	55	38	63	47	40	94
MS-2220-6	108	107	79	77	39	90	109	51	80	53	108
MS-2220-7	107	122	77	108	79	39	51	103	91	65	122
MS-2220-8	107	122	108	39	51	97	121	65	53	123	122
		Unknown Compound									
MS-2220-12	132	131	145	202	119	105	133	117	91	120	202

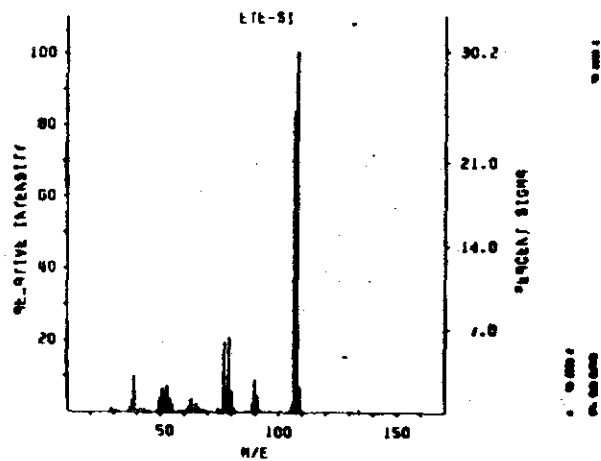


Fig. 14. Mass spectrum of suspected methyl phenol extracted from 2/71 ETE-SI - FEV fraction.

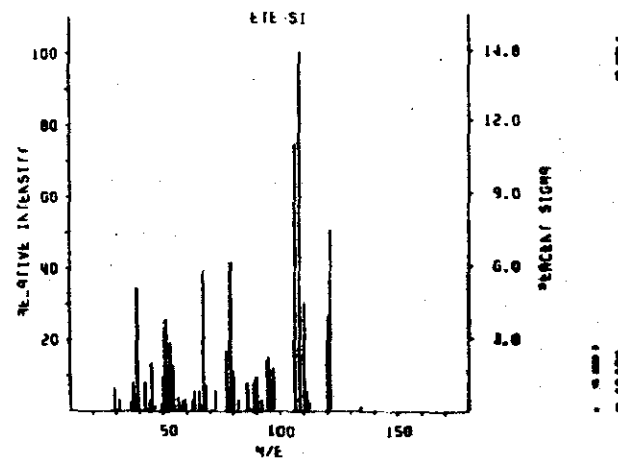


Fig. 15. Mass spectrum of suspected ethyl phenol extracted from 2/71 ETE-SI - FEV fraction.

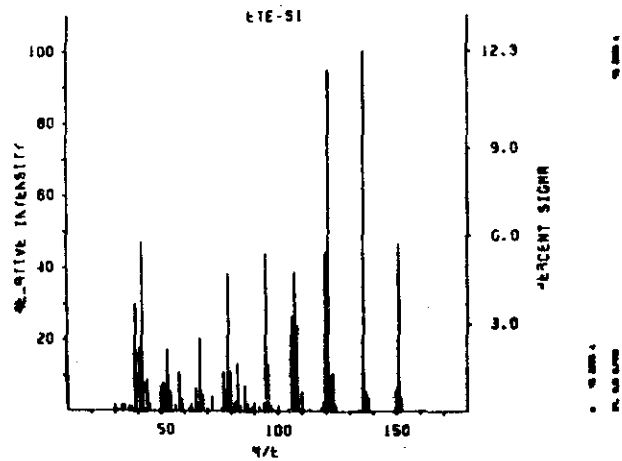


Fig. 17.

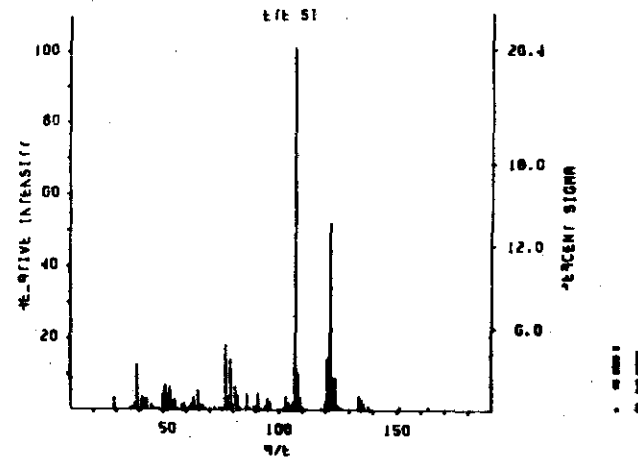


Fig. 18.

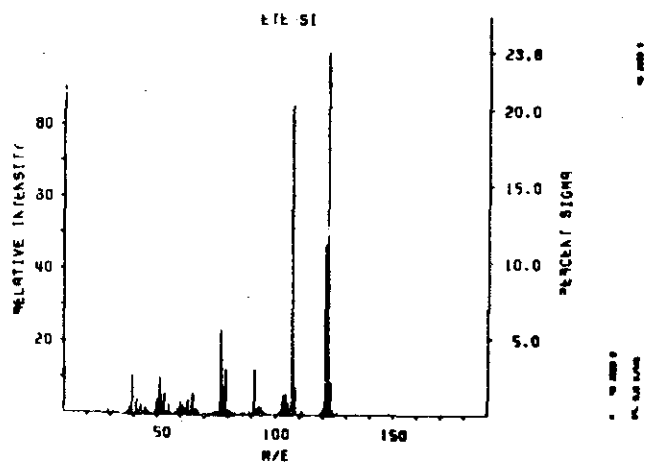


Fig. 19.

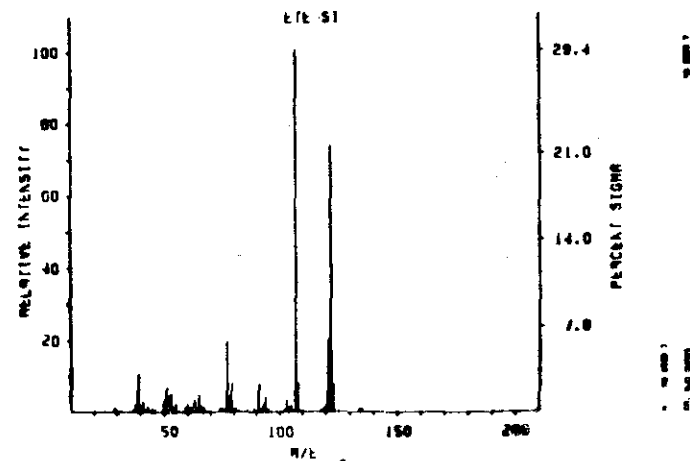


Fig. 20.

Mass spectra of unknown compounds extracted from 2/71 ETE-SI - FLV fraction.

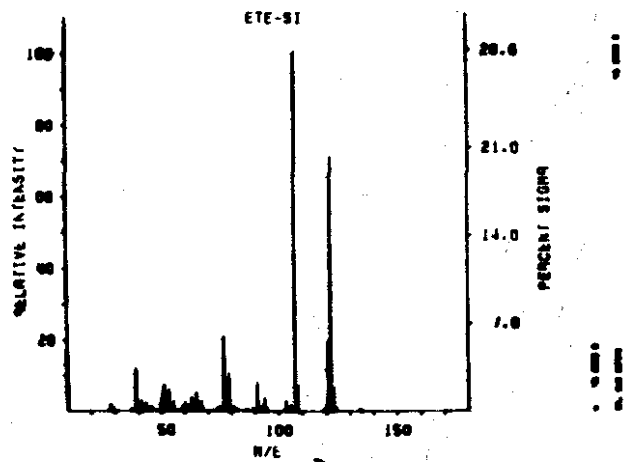


Fig. 21.

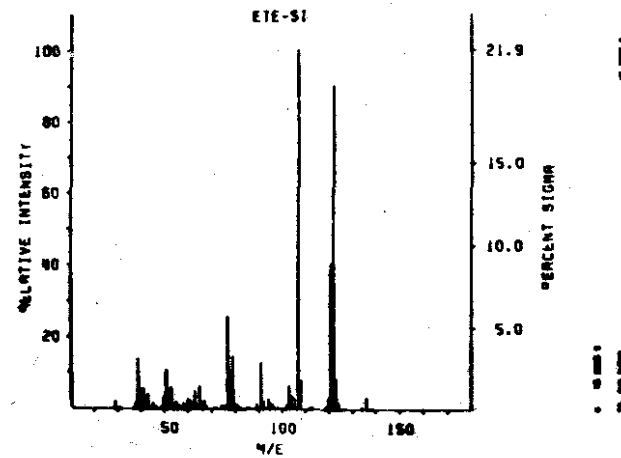


Fig. 22.

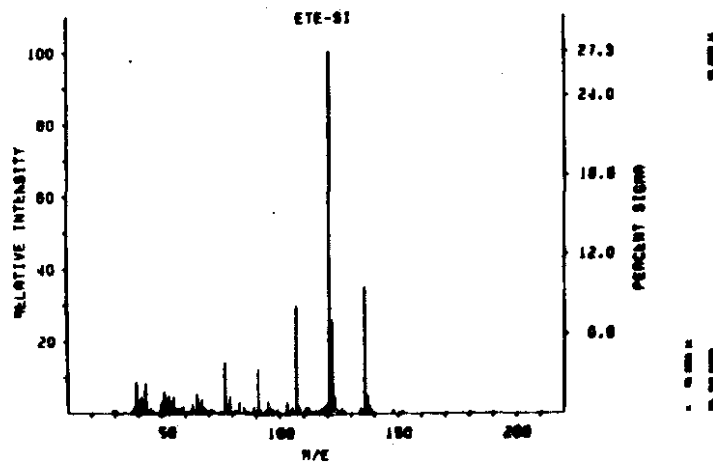
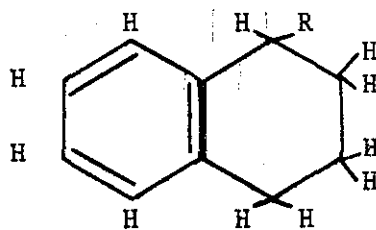


Fig. 23.

Mass spectra of suspect phenolics extracted from 2/71 ETE-SI - FEM fraction.

When informed of the phenolics in the effluent, personnel from the refinery from which this sample was taken checked to determine the source. They were able to locate the process effluent which was contributing phenolics to the final effluent and have since corrected this situation. A chromatogram of the flash volatile-methylene chloride extract of this refinery in April, 1971, indicated that the phenolics had been eliminated from the effluent.

Comparison of FEV fractions from a receiving stream (Fig. 24) approximately 38 miles downstream from a refinery outfall with that from the refinery (Fig. 25) indicates that some very persistent compounds may be discharged to the receiving stream. The complexity of the fractions, with many peaks and incomplete separation, prohibited direct GC-MS analyses. We have separated some compounds by thin layer chromatography (TLC). The FEV fractions contained such small quantities of sample that methylene chloride extracts were used for TLC separations. Chromatograms of the TLC fractions (Fig. 26) are much less complex and better GC resolution of compounds was obtained. Mass Spectrometer scan MS 2220-12 (Fig. 27) has a molecular weight (M^+) of 202, base peak 132 and other ion fragments that indicate that it has an empirical formula of $C_{15}H_{22}$. Published mass spectra of 1, 1-dimethyl-6-tert butyl-(2, 3-dihydroindene), 1, 2, 3, 4-tetrahydro-6-(1-ethyl propyl) naphthalene, and other position isomers of these compounds are very similar to MS 2220-12 but have base peaks at 131 and other differences. Additional analytical data will be needed before positive identification of MS 2220-12 can be made, but there seems to be a strong possibility that the compound may be:



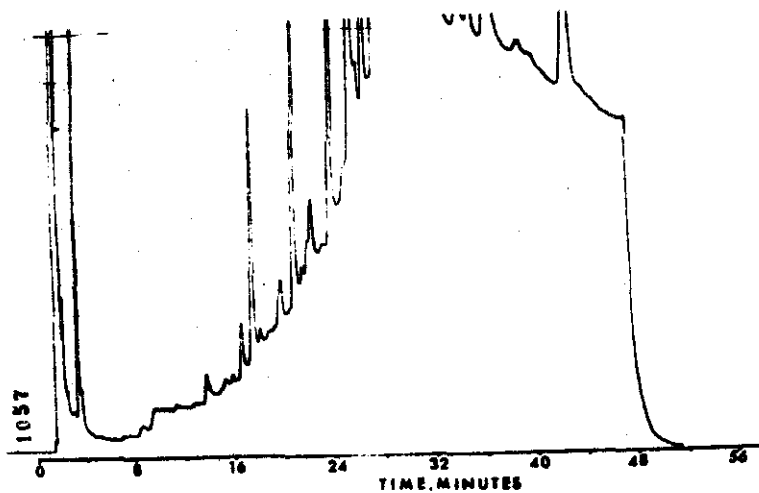


Fig. 24. Chromatogram of FEV fraction from
Skeleton Creek 1/71.

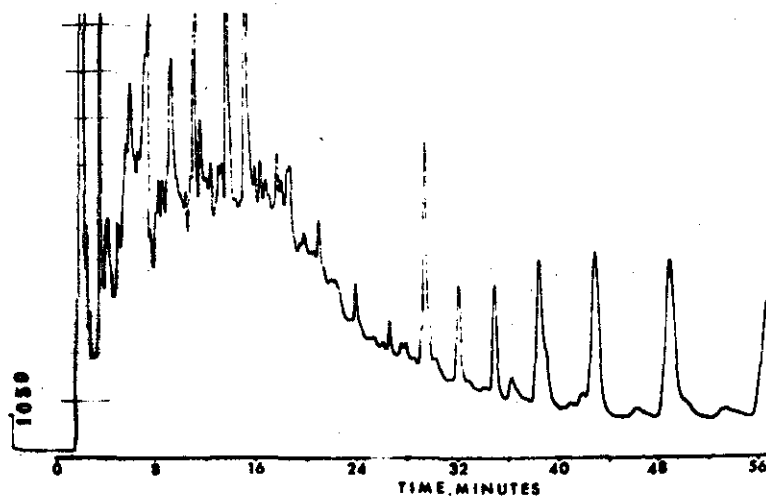


Fig. 25. Chromatogram of FEV fraction from 1/71
DFF-A.

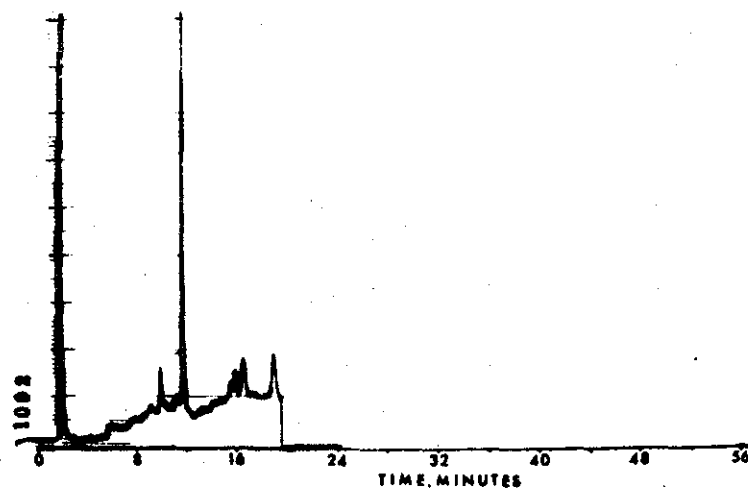


Fig. 26. Chromatogram of TLC motile fraction
from 5/71 QXP methylene chloride
solvent extract.

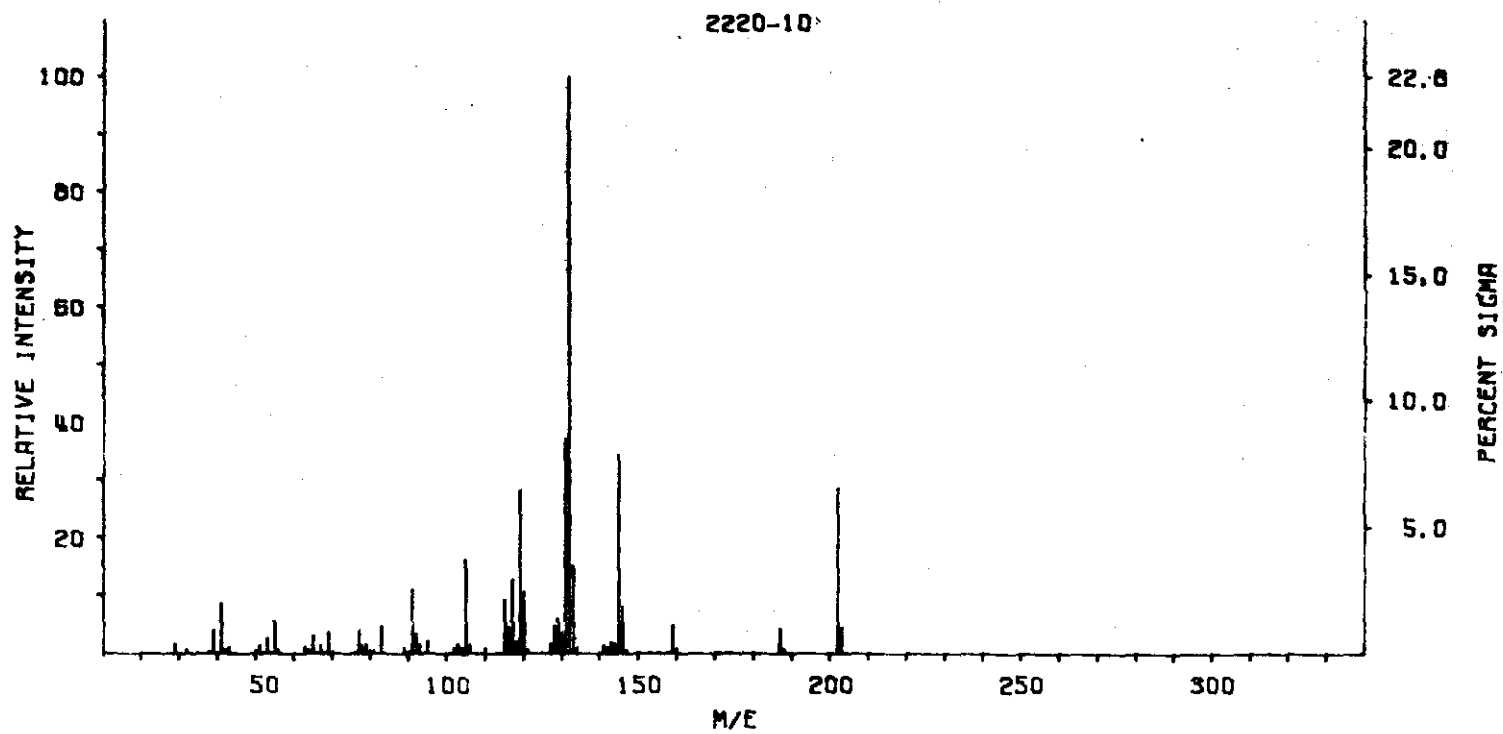


Fig. 27. Mass spectrum of unknown compound from 5/71 QXP methylene chloride solvent extract, TLC fraction number 1.

where R is a C_5H_{11} alkyl group.

The volatile portion from the continuous flash evaporation run was collected by condensing with tap water. Air was permitted to flow at a slow rate (100 ml/min) through the system, bubbling through the water condensed volatile fraction and stripping some compounds from this fraction. The air was passed up through a NuChar C-190 activated carbon column where the more volatile organic compounds were absorbed. The carbon was subsequently air dried and sequentially extracted with chloroform and 95% ethanol in a soxhlet apparatus.

The chloroform extract from the carbon exhibited five major GC peaks in association with a complex background. This sample was separated into two fractions by thin layer chromatography (methylene chloride was developing solvent, silica gel plate). The mobile fraction which migrated with the solvent front contained a homologous series of aliphatic hydrocarbons from $C_{21}H_{44}$ to $C_{25}H_{52}$ as indicated by their mass spectra. The mass spectra of MS 2897-1 through MS 2897-7 all contained major m/e fragments at 43, 57, 71, 85, 99, 113, 127, 141, 155, 169, 183, 197 etc. corresponding to an aliphatic hydrocarbon losing successive $-CH_2$ (m/e 14) fragments. The most intense m/e fragment was generally either 43 or 57 with a linear decrease in intensity at successively higher m/e fragments 14 mass units apart.

Sample Code #	M^+ (Molecular Ion)	Compound Assignment
MS 2897-1	296	$C_{21}H_{44}$
MS 2897-2	310	$C_{22}H_{46}$
MS 2897-4	324	$C_{23}H_{48}$
MS 2897-5	338	$C_{24}H_{50}$
MS 2897-7	352	$C_{25}H_{52}$

The non-motile fraction from thin layer chromatography of the carbon chloroform extract contained five major GC peaks which were scanned by mass spectrometry. Mass spectra of these compounds indicated that they were high molecular weight from 350 to >500 complex hetero atoms containing oxygen.

Atomic absorption analyses of the refinery effluents from June 1970 through January 1972 are presented in Table VIII (Appendix). In general the concentration of any individual cation analyzed was not high enough to cause acute toxicity. It is difficult to predict the long-term chronic effect of the toxic cations, copper, zinc, lead, iron, chromium, nickel, and cadmium, or to assess the potential synergistic interactions. Fathead minnow bioassays of refinery effluents indicate that in most cases (90%), 100% (non-diluted) effluent would not cause more than 50% mortality in a 96 hour static test.

The demonstrated toxicity of the volatile fraction from the flash evaporation apparatus indicates that most of the short-term acute toxicity of the refinery effluent is caused by organic substances. The heavy metals apparently were not a major contributor to acute toxicity. The pH of most refinery effluents were 7.5 to 8.5 which would tend to decrease the solubility of heavy metals. Most of the refineries treat the effluents with a series of lagoons where some of the trace heavy metals were either precipitated or chemically bound in biological tissue. Graphs of dissolved heavy metals versus suspended heavy metals from the different refineries (Figs. 28 - 47) indicate that several refineries had peaks of suspended metals in May or June and in October. The peak suspended metal concentration might correlate with algal blooms or with periods of high rainfall and runoff.

It is extremely difficult to assess all of the interactions which

can occur in a complex aqueous system such as refinery effluents.

However, some conclusions can be deduced from this research project:

1. A major contributor to the short-term acute toxicity appears to be organic compounds which can be volatilized by flash evaporation.
2. Some compounds contained in the flash evaporation fractions were identified by GC-MS as methyl or ethyl phenols and normal hydrocarbons from $C_{23}H_{48}$ (tricosane) to $C_{26}H_{54}$ (hexacosane).
3. Additional compounds scanned by mass spectrometry but not positively identified appeared to be complex high molecular weights (>300).
4. The concentration of copper, zinc, lead, chromium, nickel, cadmium and iron in the refinery effluents were below acutely toxic levels. However, the concentrations of copper, zinc, lead and chromium in the refinery effluents was high enough to possibly cause deleterious long-term effects on the aquatic organisms in the receiving stream.
5. In general, most of the refinery effluents were not toxic in short-term (96 hour) static acute toxicity bioassays. However, even the most highly treated effluents were toxic in long-term (30 days) continuous flow fathead minnow bioassays.

In summary, the present practice of biological degradation for oil refinery treatment appears to be effective in removing acute toxins but is not removing the chronic toxins. The flash evaporation procedure may potentially be utilized to remove additional volatile organic acute toxins and perhaps recycle as much as 25% of the water presently being discharged. This treatment method might also be used to remove troublesome ammonia from final effluents, reducing the nutrient load to the receiving stream.

APPENDIX

BQB #3 Oil Pond

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.31	.05	.01	.01	.02	.05	.03	.07	.02	.02	.05	.05	.12	.17	.56	.43
JUL 70	.18	.03	.01	.01	.02	.02	.05	.05	.05	.02	.09	.05	.09	.08	.49	.28
AUG 70	.09	.02	.01	.02	.04	.02	.04	.04	.04	.03	.05	.05	.03	.07	.30	.25
SEP 70	.06	.03	.01	.01	.06	.02	.08	.09	.06	.03	.08	.09	.11	.24	.46	.51
OCT 70	.17	.61	.02	.01	.02	.06	.05	1.32	.10	.03	.14	.28	.13	.95	.63	3.22
NOV 70	.04	.16	.02	.01	.03	.07	.06	.34	.10	.03	.13	.20	.17	1.22	.55	2.03
DEC 70	.07	.16	.02	.01	.02	.05	.05	.50	.11	.02	.10	.13	.19	.98	.56	1.85
JAN 71	.06	.06	.02	.01	.03	.04	.10	.16	.14	.03	.23	.07	.11	.39	.69	.76
FEB 71	.06	.13	.04	.01	.08	.06	.08	.78	.04	.03	.15	.07	.17	.60	.62	1.68
\bar{X}	.12	.14	.01	.01	.04	.04	.06	.37	.07	.02	.11	.11	.23	.52		
Hi	.31	.61	.04	.02	.08	.07	.10	1.32	.14	.03	.23	.28	.19	1.22		
Lo	.04	.02	.01	.01	.02	.02	.03	.04	.02	.02	.05	.05	.09	.07		

d = dissolved s = suspended

Table VIII. (Continued)

BQB #4 Oxid. Pond

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.11	.02	.01	.01	.02	.02	.03	.03	.04	.02	.07	.07	.22	.05	.50	.24
JUL 70	.05	.01	.02	.01	.02	.02	.03	.03	.03	.02	.07	.05	.09	.05	.31	.21
AUG 70	.04	.03	.01	.01	.09	.02	.05	.03	.03	.03	.05	.05	.08	.11	.35	.28
SEP 70	.06	.01	.01	.01	.04	.02	.07	.06	.03	.03	.10	.06	.26	.06	.57	.25
OCT 70	.13	.01	.02	.01	.03	.02	.05	.23	.06	.03	.27	.06	.15	.26	.71	.62
NOV 70	.07	.02	.02	.01	.03	.03	.06	.11	.07	.03	.20	.05	.11	.42	.56	.67
DEC 70	.07	.05	.01	.01	.03	.05	.07	.17	.06	.03	.12	.04	.09	.36	.45	.71
JAN 71	.04	.06	.02	.01	.03	.04	.03	.12	.13	.03	.16	.05	.14	.48	.55	.79
FEB 71	.05	.07	.01	.01	.02	.02	.08	.36	.03	.03	.10	.05	.11	.16	.40	.70
\bar{X}	.07	.03	.01	.01	.03	.03	.05	.13	.05	.03	.13	.05	.14	.22		
Hi	.13	.07	.02	.01	.09	.05	.08	.36	.13	.03	.27	.07	.26	.48		
Lo	.04	.01	.01	.01	.02	.02	.03	.03	.03	.02	.05	.05	.08	.05		

d = dissolved s = suspended

Table VIII. (Continued)

BQD-North

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.03	.03	.01	.01	.08	.02	.05	.03	.08	.02	.07	.05	.25	1.16	.57	1.33
JUL 70	.04	.01	.02	.01	.02	.02	.03	.03	.03	.02	.06	.05	.12	.33	.32	.49
AUG 70	.05	.05	.02	.01	.03	.02	.08	.03	.05	.03	.05	.05	.22	.12	.50	.31
SEP 70	.07	.02	.01	.01	.04	.03	.13	.07	.06	.03	.21	.08	.12	.81	.64	1.05
OCT 70	.03	.02	.04	.01	.04	.03	.11	.08	.14	.03	.30	.05	.25	.75	.91	.97
NOV 70	.04	.02	.03	.01	.04	.03	.05	.09	.08	.02	.32	.06	.56	.87	1.12	1.10
DEC 70	.05	.36	.02	.01	.05	.05	.08	.11	.09	.02	.13	.03	.35	.60	.77	1.18
JAN 71	.05	.04	.03	.01	.02	.02	.12	.22	.05	.03	.19	.05	.15	.74	.61	1.11
FEB 71	.04	.10	.01	.01	.02	.02	.05	.57	.05	.03	.10	.05	.06	.65	.33	1.43
\bar{X}	.04	.07	.01	.01	.04	.02	.07	.14	.07	.02	.15	.05	.23	.67		
Hi	.07	.36	.04	.01	.08	.05	.13	.57	.14	.03	.32	.08	.56	1.16		
Lo	.03	.01	.01	.01	.02	.02	.03	.03	.03	.02	.07	.03	.06	.12		

d = dissolved s = suspended

Table VIII. Concentration (mg/l) of toxic heavy metals in monthly oil refinery effluent samples.

BQD-South

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70	.19	.03	.01	.01	.06	.02	.06	.03	.03	.02	.06	.05	.46	.28	.87	.44
JUL 70	.02	.01	.02	.01	.02	.02	.06	.03	.02	.02	.12	.05	.06	.32	.32	.46
AUG 70	.04	.03	.01	.01	.02	.02	.06	.04	.03	.03	.05	.05	.12	.20	.33	.38
SEP 70	.11	.03	.02	.01	.03	.02	.11	.11	.06	.03	.14	.06	.35	.66	.82	.92
OCT 70	.05	.02	.27	.02	.05	.05	.06	.09	.12	.03	.31	.06	.61	.90	1.47	1.17
NOV 70	.04	.04	.02	.01	.03	.02	.05	.09	.09	.02	.22	.05	.15	.57	.60	.80
DEC 70	.04	.02	.02	.01	.04	.05	.05	.09	.07	.02	.18	.04	.12	.65	.52	.88
JAN 71	.02	.02	.03	.01	.03	.02	.04	.14	.10	.03	.12	.05	.93	.38	1.27	.65
FEB 71	.02	.02	.01	.01	.02	.02	.03	.28	.02	.03	.15	.05	.29	.29	.54	.60
\bar{X}	.06	.02	.04	.01	.04	.06	.06	.09	.06	.02	.15	.04	.34	.47		
Hi	.19	.04	.27	.02	.06	.05	.11	.28	.12	.03	.22	.06	.93	.90		
Lo	.02	.02	.01	.01	.02	.02	.03	.03	.02	.02	.06	.04	.06	.20		

d = dissolved s = suspended

Table VIII. (Continued)

DPF-A

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.22	.03	.01	.01	.09	.02	.05	.03	.04	.02	.06	.05	.16	.15	.63	.32
JUL 70	.04	.01	.01	.01	.02	.02	.08	.03	.04	.02	.16	.05	.06	.05	.41	.21
AUG 70	.07	.04	.01	.04	.03	.02	.04	.03	.03	.03	.05	.05	.10	.08	.33	.29
SEP 70	.09	.03	.01	.01	.05	.02	.08	.06	.03	.03	.10	.05	.18	.06	.54	.26
OCT 70	.05	.14	.04	.01	.04	.04	.06	.17	.11	.07	.23	.05	.15	.48	.68	.96
NOV 70	.03	.05	.03	.01	.03	.04	.04	.09	.07	.02	.15	.07	.26	.45	.61	.73
DEC 70	.06	.16	.02	.01	.03	.08	.05	.13	.08	.02	.13	.07	.24	.62	.61	1.09
JAN 71	.05	.02	.01	.01	.04	.02	.03	.15	.03	.03	.12	.05	.31	.29	.59	.57
FEB 71	.08	.06	.01	.01	.02	.04	.03	.17	.03	.03	.08	.07	.20	.54	.45	.92
\bar{X}	.08	.07	.02	.01	.04	.03	.05	.10	.05	.03	.12	.06	.18	.30		
Hi	.22	.16	.04	.04	.05	.08	.08	.17	.11	.07	.23	.07	.31	.62		
Lo	.03	.02	.01	.01	.02	.02	.03	.03	.03	.02	.06	.05	.06	.05		

d = dissolved s = suspended

Table VIII. (Continued)

DPF-B

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70																
JUL 70	.03	.01	.01	.01	.02	.02	.05	.03	.05	.02	.06	.05	.16	.16	.38	.34
AUG 70	.06	.03	.01	.03	.02	.02	.04	.03	.03	.03	.12	.05	.12	.08	.40	.27
SEP 70	.10	.04	.01	.01	.04	.03	.09	.07	.04	.03	.09	.05	.19	.21	.56	.44
OCT 70	.50	.20	.02	.01	.07	.17	.05	.14	.10	.03	.21	.05	.35	.39	1.30	.99
NOV 70	.04	.14	.02	.01	.04	.08	.04	.08	.06	.02	.18	.06	.23	.89	.61	.28
DEC 70	.03	.10	.01	.01	.04	.06	.07	.09	.09	.03	.07	.05	.08	.70	.39	1.02
JAN 71																
FEB 71	.06	.04	.02	.01	.02	.03	.03	.18	.07	.03	.05	.10	.30	.56	.55	.93
\bar{X}	.11	.08	.01	.01	.04	.06	.05	.09	.06	.03	.11	.04	.16	.43		
Hi	.50	.20	.02	.03	.07	.17	.09	.14	.10	.03	.21	.06	.35	.89		
Lo	.03	.01	.01	.01	.02	.02	.03	.03	.03	.02	.05	.05	.08	.08		

d = dissolved s = suspended

Table VIII. (Continued)

DPF-C

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70																
JUL 70																
AUG 70																
SEP 70																
OCT 70																
NOV 70																
DEC 70																
JAN 71																
FEB 71	.03	.03	.01	.01	.02	.02	.03	.20	.05	.03	.10	.05	.13	.09	.37	.43
\bar{X}	.03	.03	.01	.01	.02	.02	.03	.20	.05	.03	.10	.05	.13	.09		
Hi	.03	.03	.01	.01	.02	.02	.03	.20	.05	.03	.10	.05	.13	.09		
Lo	.03	.03	.01	.01	.02	.02	.03	.20	.05	.03	.10	.05	.13	.09		

d = dissolved s = suspended

Table VIII. (Continued)

DPQ Holding Pond

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.08	.03	.02	.01	.06	.02	.06	.03	.02	.02	.12	.05	.18	.24	.54	.41
JUL 70	.19	.07	.02	.01	.02	.05	.03	.24	.03	.02	.06	.05	.08	.53	.43	.98
AUG 70	.06	.04	.02	.02	.02	.02	.08	.04	.04	.02	.05	.05	.08	.24	.35	.44
SEP 70	.07	.02	.01	.01	.02	.02	.08	.09	.04	.02	.11	.05	.18	.23	.51	.45
OCT 70	.04	.06	.01	.01	.02	.06	.03	.45	.08	.02	.20	.12	.13	.71	.51	1.44
NOV 70	.05	.02	.01	.01	.02	.03	.04	.15	.17	.02	.17	.08	.18	.86	.64	1.17
DEC 70	.07	.12	.02	.01	.02	.06	.03	.22	.08	.02	.16	.08	.24	.68	.62	1.19
JAN 71	.02	.02	.01	.01	.04	.03	.08	.17	.07	.02	.17	.06	.67	.34	1.06	.66
FEB 71	.10	.30	.01	.01	.02	.11	.04	1.70	.06	.03	.05	.22	.12	1.10	.40	3.47
\bar{X}	.07	.07	.01	.01	.03	.04	.05	.32	.06	.02	.12	.08	.21	.49		
Hi	.19	.30	.02	.02	.06	.11	.08	1.70	.17	.02	.20	.22	.67	1.10		
Lo	.02	.02	.01	.01	.02	.02	.03	.03	.02	.02	.05	.05	.08	.23		

d = dissolved s = suspended

Table VIII. (Continued)

DPQ Refinery Outfall

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70																
JUL 70	.06	.01	.02	.01	.02	.02	.09	.03	.02	.02	.11	.05	.05	.11	.37	.27
AUG 70	.16	.03	.02	.01	.03	.02	.07	.04	.03	.02	.05	.05	.12	.12	.48	.30
SEP 70	.09	.02	.01	.01	.03	.03	.11	.10	.03	.02	.08	.05	.19	.64	.54	.88
OCT 70	.10	.06	.02	.01	.02	.04	.04	.21	.10	.02	.19	.06	.13	.54	.60	.95
NOV 70	.04	.03	.02	.01	.03	.03	.04	.10	.09	.02	.13	.07	.18	.28	.53	.54
DEC 70	.09	.06	.01	.01	.03	.04	.06	.19	.08	.02	.10	.06	.35	.98	.72	1.36
JAN 71	.05	.20	.01	.01	.04	.12	.10	.10	.06	.03	.15	.07	.15	.78	.56	1.31
FEB 71	.22	.13	.14	.01	.05	.05	.03	1.20	.06	.03	.07	.15	.44	1.10	1.01	2.67
\bar{X}	.10	.07	.02	.01	.03	.04	.07	.25	.06	.02	.11	.07	.20	.57		
Hi	.22	.20	.14	.01	.05	.12	.11	1.20	.10	.03	.19	.15	.44	1.10		
Lo	.04	.01	.01	.01	.02	.02	.03	.03	.02	.02	.05	.05	.05	.11		

d = dissolved s = suspended

Table VIII. (Continued)

ETE-SI

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.13	.03	.01	.01	.07	.05	.06	.03	.02	.02	.07	.05	.35	.42	.71	.61
JUL 70	.05	.02	.02	.01	.02	.02	.09	.04	.02	.03	.05	.05	.23	.17	.48	.34
AUG 70	.05	.05	.01	.01	.03	.02	.05	.06	.03	.03	.05	.05	.59	.78	.81	1.00
SEP 70	.06	.02	.01	.01	.02	.02	.07	.08	.10	.03	.05	.05	.60	.54	.91	.75
OCT 70	.02	.13	.06	.01	.02	.07	.06	.24	.07	.03	.21	.10	.51	1.45	.95	2.03
NOV 70	.03	.03	.04	.01	.04	.03	.04	.14	.15	.03	.28	.06	.96	.76	1.51	1.06
DEC 70	.04	.03	.03	.01	.02	.02	.04	.08	.09	.02	.15	.05	.65	.40	1.02	.61
JAN 71	.01	.16	.01	.01	.02	.07	.03	.39	.08	.03	.08	.18	2.47	.65	2.70	1.49
FEB 71	.02	.03	.01	.01	.03	.02	.05	.38	.05	.03	.05	.13	.75	.53	.96	1.13
\bar{X}	.04	.05	.02	.01	.03	.03	.05	.16	.06	.02	.11	.08	.79	.63		
Hi	.13	.16	.06	.01	.07	.07	.09	.39	.15	.03	.28	.18	2.47	1.45		
Lo	.01	.02	.01	.01	.02	.02	.03	.03	.02	.02	.05	.05	.23	.17		

d = dissolved s = suspended

Table VIII. (Continued)

ETE SJ

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70	.10	.03	.02	.01	.02	.03	.03	.03	.10	.02	.06	.05	.15	.07	.48	.24
JUL 70	.11	.01	.03	.01	.03	.02	.03	.03	.40	.02	.05	.05	.05	.05	.70	.19
AUG 70	.03	.10	.01	.02	.02	.03	.05	.05	.07	.03	.05	.05	.19	.20	.42	.48
SEP 70	.08	.02	.02	.02	.03	.02	.08	.09	.23	.03	.05	.05	.10	.23	.59	.46
OCT 70	.04	.03	.03	.01	.02	.02	.05	.11	.10	.03	.28	.05	.09	.27	.61	.52
NOV 70	.07	.03	.02	.01	.02	.02	.04	.11	.09	.03	.13	.10	.13	.25	.50	.55
DEC 70	.09	.05	.03	.01	.02	.02	.04	.11	.08	.02	.07	.02	.22	.47	.55	.70
JAN 71	.06	.04	.02	.01	.02	.05	.03	.17	.08	.03	.10	.05	.14	.89	.45	1.24
FEB 71	.07	.06	.01	.01	.02	.03	.03	.36	.13	.03	.05	.05	.09	.27	.40	.81
\bar{X}	.07	.04	.02	.01	.02	.02	.04	.11	.14	.02	.09	.05	.12	.30		
Hi	.11	.10	.03	.02	.03	.05	.08	.36	.40	.03	.28	.10	.22	.89		
Lo	.03	.01	.01	.02	.02	.02	.03	.03	.40	.03	.28	.10	.05	.05		

d = dissolved s = suspended

Table VIII. (Continued)

ETE SK

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.28	.10	.01	.02	.07	.02	.06	.03	.08	.02	.10	.05	.22	.59	.82	.83
JUL 70	.04	.02	.03	.01	.02	.02	.12	.10	.31	.03	.05	.05	.06	.11	.63	.34
AUG 70	.11	.05	.03	.02	.02	.02	.06	.04	.06	.03	.07	.05	.13	.10	.48	.31
SEP 70	.09	.02	.01	.01	.02	.02	.08	.06	.04	.03	.06	.07	.48	1.02	.78	1.23
OCT 70	.12	.10	.02	.01	.02	.04	.05	.14	.10	.05	.19	.08	.26	.53	.76	.95
NOV 70	.06	.07	.03	.01	.03	.02	.04	.10	.08	.03	.16	.07	.31	.68	.71	.98
DEC 70	.04	.09	.02	.01	.02	.02	.03	.13	.07	.02	.08	.05	.28	.80	.54	1.12
JAN 71	.06	.15	.01	.01	.02	.07	.03	.20	.08	.03	.12	.05	.54	2.94	.86	3.45
FEB 71	.05	.02	.01	.01	.02	.02	.03	.27	.09	.03	.05	.05	.51	.42	.76	.82
\bar{X}	.09	.06	.01	.01	.02	.02	.05	.11	.10	.03	.09	.05	.31	.79		
Hi	.28	.15	.03	.02	.07	.07	.12	.20	.31	.05	.19	.08	.54	2.94		
Lo	.04	.02	.01	.01	.02	.02	.03	.03	.07	.02	.05	.05	.06	.10		

d = dissolved s = suspended

Table VIII. (Continued)

ETU-60.10

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.10	.03	.01	.01	.06	.02	.05	.03	.02	.02	.05	.05	.26	.05	.55	.21
JUL 70	.02	.02	.01	.01	.02	.02	.05	.03	.03	.02	.05	.05	.12	.08	.30	.23
AUG 70	.03	.07	.01	.01	.03	.02	.06	.15	.04	.03	.05	.05	.09	.15	.31	.48
SEP 70	.08	.01	.01	.01	.02	.02	.09	.16	.04	.03	.10	.09	.35	.19	.69	.51
OCT 70	.04	.09	.02	.02	.07	.02	.06	.56	.08	.03	.22	.11	.20	.27	.59	1.10
NOV 70	.02	.04	.02	.01	.02	.02	.37	.11	.07	.03	.20	.10	.32	.26	1.02	.57
DEC 70	.02	.07	.02	.01	.02	.03	.09	.30	.06	.02	.10	.03	.16	.28	.47	.74
JAN 71	.01	.03	.01	.01	.02	.02	.08	.04	.03	.03	.12	.06	.26	4.32	.53	4.51
FEB 71	.02	.03	.01	.01	.04	.02	.06	.42	.06	.03	.05	.05	.17	.17	.41	.73
\bar{X}	.03	.04	.01	.01	.03	.02	.11	.20	.04	.02	.10	.06	.21	.64		
Hi	.10	.09	.02	.02	.07	.03	.37	.56	.08	.03	.22	.11	.35	4.32		
Lo	.01	.01	.01	.01	.02	.02	.05	.03	.02	.02	.05	.03	.12	.05		

d = dissolved s = suspended

Table VIII. (Continued)

LND-North

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70																
JUL 70																
AUG 70	.09	.05	.01	.01	.03	.02	.05	.04	.04	.03	.05	.05	.16	.34	.43	.54
SEP 70																
OCT 70	.02	.11	.02	.01	.02	.02	.05	.12	.06	.03	.19	.13	1.50	1.80	1.84	2.22
NOV 70	.04	.11	.03	.01	.03	.03	.04	.16	.05	.02	.16	.16	.19	2.30	.54	2.89
DEC 70	.04	.27	.02	.01	.03	.09	.04	.24	.08	.03	.18	.36	.87	2.71	1.26	3.71
JAN 71	.02	.02	.01	.01	.03	.03	.04	.03	.06	.03	.10	.05	1.22	.15	1.48	.32
FEB 71	.04	.23	.01	.01	.02	.03	.05	.39	.06	.03	.10	.10	.06	2.00	.34	2.79
\bar{X}	.04	.13	.01	.01	.02	.03	.04	.16	.05	.02	.13	.14	.66	1.55		
Hi	.09	.27	.03	.01	.03	.09	.05	.39	.08	.03	.19	.36	1.50	2.71		
Lo	.02	.02	.01	.01	.02	.02	.04	.03	.04	.02	.05	.05	.06	.15		

d = dissolved s = suspended

Table VIII. (Continued)

LND-South

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70																
JUL 70																
AUG 70	.03	.02	.01	.01	.02	.02	.05	.04	.04	.03	.05	.05	.13	.24	.33	.41
SEP 70																
OCT 70	.02	.01	.01	.01	.02	.02	.05	.06	.05	.03	.21	.05	.14	.80	.50	.98
NOV 70	.04	.04	.02	.01	.04	.04	.03	.12	.11	.03	.15	.08	.15	1.95	.44	2.27
DEC 70	.03	.05	.01	.01	.03	.03	.04	.14	.07	.03	.14	.11	.16	2.54	.48	2.91
JAN 71	.02	.11	.01	.01	.03	.03	.03	.03	.06	.03	.06	.07	.10	.51	.31	.79
FEB 71	.03	.13	.01	.01	.02	.02	.03	.25	.03	.03	.10	.05	.08	2.00	.30	2.49
\bar{X}	.02	.06	.01	.01	.05	.05	.03	.10	.06	.03	.11	.06	.12	1.34		
Hi	.04	.13	.02	.01	.04	.04	.05	.25	.11	.03	.21	.11	.16	2.54		
Lo	.02	.01	.01	.01	.02	.02	.03	.03	.03	.03	.05	.05	.08	.51		

d = dissolved s = suspended

Table VIII. (Continued)

LNX

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70	.05	.03	.01	.01	.02	.04	.05	.13	.03	.02	.05	.05	.07	.20	.28	.48
JUL 70	.06	.01	.01	.01	.06	.02	.03	.03	.06	.02	.05	.05	.05	.05	.32	.19
AUG 70	.11	.05	.02	.01	.03	.02	.04	.16	.04	.03	.08	.07	.06	.20	.38	.54
SEP 70																
OCT 70	.07	.02	.01	.01	.02	.03	.04	.24	.08	.03	.28	.05	.15	.23	.65	.61
NOV 70	.05	.08	.02	.01	.03	.08	.03	.39	.07	.03	.29	.07	.20	.92	.69	1.58
DEC 70	.21	.07	.02	.01	.07	.02	.04	.20	.05	.02	.10	.03	.37	.24	.86	.59
JAN 71	.01	.03	.02	.01	.02	.02	.03	.03	.03	.03	.13	.08	.07	.73	.31	.93
FEB 71	.06	.02	.01	.01	.02	.02	.04	.36	.03	.05	.09	.05	.14	.20	.39	.71
\bar{X}	.08	.04	.02	.01	.03	.03	.04	.20	.05	.03	.13	.06	.14	.35		
Hi	.21	.08	.02	.01	.07	.08	.05	.39	.08	.05	.29	.08	.37	.92		
Lo	.01	.01	.01	.01	.02	.02	.03	.03	.03	.02	.05	.03	.05	.05		

d = dissolved s = suspended

Table VIII. (Continued)

NDD

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70	.16	.03	.01	.01	.06	.02	.03	.03	.02	.02	.08	.05	.15	.12	.51	.28
JUL 70	.02	.02	.02	.01	.02	.02	.06	.03	.02	.02	.11	.05	.03	.33	.28	.48
AUG 70	.05	.02	.02	.02	.03	.02	.05	.08	.03	.03	.07	.05	.23	.26	.48	.48
SEP 70	.06	.02	.01	.01	.02	.02	.08	.09	.03	.03	.08	.05	.19	.12	.47	.34
OCT 70	.07	.02	.02	.01	.02	.02	.03	.14	.03	.03	.21	.06	.09	1.07	.47	1.35
NOV 70	.03	.03	.03	.01	.04	.03	.04	.15	.04	.02	.17	.08	.16	.69	.51	1.01
DEC 70	.02	.07	.02	.01	.02	.03	.03	.42	.04	.02	.18	.03	.20	.63	.51	1.21
JAN 71	.03	.04	.01	.01	.02	.02	.03	.06	.03	.03	.12	.05	.52	.47	.76	.68
FEB 71	.03	.13	.01	.01	.02	.02	.03	1.10	.06	.03	.12	.05	.11	.88	.38	2.22
\bar{X}	.05	.04	.02	.01	.03	.09	.04	.23	.03	.02	.13	.05	.21	.51		
Hi	.16	.13	.03	.02	.06	.03	.08	1.10	.06	.03	.21	.08	.52	1.07		
Lo	.02	.02	.01	.01	.02	.02	.03	.03	.02	.02	.07	.05	.03	.12		

d = dissolved s = suspended

Table VIII. (Continued)

TSQ Stream Below

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
JUN 70	.13	.02	.01	.01	.10	.04	.03	.03	.03	.02	.05	.05	.10	.05	.45	.22
JUL 70	.02	.01	.01	.01	.02	.02	.03	.03	.02	.02	.12	.05	.05	.05	.27	.21
AUG 70	.03	.03	.01	.01	.03	.02	.05	.03	.03	.03	.05	.05	.07	.58	.27	.75
SEP 70																
OCT 70	.02	.02	.01	.01	.03	.02	.04	.10	.07	.03	.13	.05	.03	2.12	.38	2.35
NOV 70	.04	.06	.02	.01	.04	.03	.07	.09	.06	.02	.13	.04	.12	1.16	.48	1.41
DEC 70	.03	.02	.03	.01	.04	.02	.09	.11	.06	.01	.13	.03	.13	.15	.51	.36
JAN 71	.01	.12	.01	.01	.02	.03	.04	.03	.06	.03	.16	.05	.10	.45	.40	.72
FEB 71	.01	.02	.01	.01	.05	.02	.03	.24	.03	.03	.05	.05	.11	.20	.29	.57
\bar{X}	.03	.03	.01	.01	.04	.02	.04	.08	.04	.02	.10	.05	.09	.59		
Hi	.13	.12	.03	.01	.10	.04	.09	.24	.07	.03	.16	.05	.13	2.12		
Lo	.01	.01	.01	.01	.02	.02	.03	.03	.02	.01	.05	.03	.05	.05		

d = dissolved s = suspended

Table VIII. (Continued)

TSQ Plant Effluent

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.05	.01	.01	.01	.02	.02	1.27	.03	.02	.02	.22	.07	.05	.05	1.64	.23
JUL 70																
AUG 70	.08	.02	.01	.01	.03	.02	1.08	.04	.04	.03	.08	.05	.03	.05	1.35	.22
SEP 70	.06	.01	.01	.01	.04	.02	1.20	.06	.04	.03	.09	.07	.24	.12	1.68	.32
OCT 70	.03	.12	.02	.01	.03	.05	.68	1.44	.10	.03	.22	2.08	.14	1.18	1.22	4.91
NOV 70	.03	.07	.02	.01	.04	.04	.81	.19	.06	.02	.16	.24	.13	.81	1.25	.58
DEC 70	.05	.02	.03	.01	.05	.02	1.09	.11	.07	.02	.14	.08	.16	.14	1.59	.40
JAN 71	.02	.11	.02	.01	.02	.04	.75	.03	.10	.03	.14	.22	.10	.74	1.15	1.18
FEB 71	.05	.08	.04	.01	.03	.02	.38	.51	.09	.03	.05	.05	.17	.21	.81	.91
\bar{X}	.04	.06	.02	.01	.03	.03	.91	.28	.06	.02	.12	.32	.12	.37		
Hi	.08	.12	.04	.01	.05	.05	1.27	1.44	.10	.03	.22	2.08	.24	1.18		
Lo	.02	.01	.01	.01	.02	.02	.38	.03	.02	.02	.05	.05	.03	.05		

d = dissolved s = suspended

Table VIII. (Continued)

QXP

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.07	.01	.01	.01	.05	.02	.03	.03	.05	.02	.06	.07	.12	.05	.39	.22
JUL 70	.13	.01	.01	.01	.02	.02	.08	.03	.03	.02	.06	.05	.05	.05	.38	.21
AUG 70	.20	.07	.01	.01	.02	.02	.05	.09	.03	.03	.05	.06	.10	.20	.46	.48
SEP 70	.13	.01	.01	.01	.02	.02	.07	.09	.03	.03	.06	.06	.13	.06	.45	.28
OCT 70	.11	.18	.02	.01	.04	.02	.06	.12	.08	.03	.18	.05	.10	.25	.49	.76
NOV 70																
DEC 70	.11	.11	.02	.01	.04	.03	.05	.09	.07	.02	.13	.04	.12	.26	.54	.56
JAN 71	.14	.04	.05	.01	.03	.02	.06	.03	.04	.03	.06	.05	.20	2.34	.58	2.52
FEB 71	.14	.03	.01	.01	.02	.02	.03	.33	.03	.03	.03	.14	.11	.57	.37	1.13
\bar{X}	.16	.05	.01	.01	.03	.02	.05	.08	.04	.02	.08	.06	.10	.42		
Hi	.20	.18	.05	.01	.05	.03	.08	.33	.08	.03	.18	.14	.20	2.34		
Lo	.07	.01	.01	.01	.02	.02	.03	.03	.03	.02	.03	.05	.05	.05		

d = dissolved s = suspended

Table VIII. (Continued)

UWU

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
JUN 70	.07	.12	.01	.01	.06	.12	.03	.03	.03	.02	.05	.06	.66	1.70	.91	2.06
JUL 70	.03	.06	.01	.01	.02	.03	.03	.03	.02	.02	.22	.07	.32	.06	.65	.29
AUG 70	.34	.10	.02	.01	.09	.12	.03	.05	.03	.03	.07	.12	.13	.59	.71	1.02
SEP 70	.12	.13	.01	.01	.03	.02	.04	.08	.03	.03	.09	.10	.25	.13	.57	.50
OCT 70	.08	.35	.02	.01	.02	.19	.03	.12	.06	.03	.18	.12	1.29	1.52	1.68	2.34
NOV 70	.08	.29	.02	.01	.02	.16	.03	.13	.06	.02	.19	.18	.45	.73	.85	1.52
DEC 70	.33	.19	.02	.01	.02	.11	.02	.11	.04	.02	.08	.28	.65	.63	1.16	1.35
JAN 71	.08	.02	.01	.01	.04	.03	.03	.03	.03	.03	.06	.05	.31	.17	.56	.34
FEB 71	.29	.29	.01	.01	.02	.11	.03	.25	.05	.03	.07	.07	.29	1.63	.76	2.39
\bar{X}	.16	.15	.01	.01	.03	.10	.03	.08	.04	.02	.10	.12	.48	.79		
H1	.34	.35	.02	.01	.09	.19	.04	.25	.06	.03	.19	.28	1.29	1.63		
Lo	.03	.02	.01	.01	.02	.02	.02	.03	.02	.02	.05	.05	.13	.06		

d = dissolved s = suspended

Table VIII. (Continued)

BQB 3

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Σd</u>	<u>Σs</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.03	.13	.006	.002	.02	.03	.08	.15	.01	.00	.15	.28	.12	.48	.41	1.08
MAY 71	.07	.19	.012	.002	.0	.06	.04	.50	.06	.01	.03	.36	.08	1.30	.29	2.4
JUN 71	.10	.17	.006	.001	.02	.07	.05	.50	.04	.006	.10	.26	.12	1.1	.35	2.1
JUL 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
AUG 71	.22	.10	.004	0	.03	.05	0	.17	.02	.009	.14	.05	.10	.04	.51	.42
SEP 71	.02	.09	.01	0	.03	.05	0	.52	.04	.003	.05	.01	.21	.64	.36	1.3
OCT 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
NOV 71	.02	.04	.02	0	.03	.04	---	---	.09	.03	.05	.13	.08	.23	.29	.47
JAN 72	.11	.05	.004	.001	.03	.04	.04	.02	.02	.01	0	.15	.08	.38	.28	.65
\bar{x}	.08	.09	.009	.001	.02	.06	.04	.31	.04	.008	.08	.18	.11	.59		
Hi	.22	.19	.02	.002	.03	.07	.08	.52	.09	.03	.15	.36	.21	1.3		
Lo	.02	.05	.004	0	0	.03	0	.02	.01	0	0	.01	.08	.04		

d = dissolved s = suspended

Table VIII. Concentration (mg/l) of toxic heavy metals in monthly oil refinery effluent samples.

BQB 4

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Ed</u>	<u>Es</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.03	.13	.006	.002	.02	.03	.02	.02	.02	0	.25	.01	.18	.09	.62	.32
MAY 71	.03	.20	.01	.001	0	.02	.06	.06	.03	.005	0	.02	.10	.19	.22	.50
JUN 71	.02	.17	.006	0	.03	.03	0	.06	.02	.01	.10	.01	0	.16	.17	.38
JUL 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
AUG 71	.64	.02	.006	0	.03	.01	.02	.01	.01	.003	.08	0	.17	0	.96	.64
SEP 71	.01	.01	.008	0	.03	.03	0	.02	.04	0	.05	0	.11	.07	.25	.13
OCT 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
NOV 71	.05	0	.006	0	.03	.01	---	---	.07	.02	.07	0	.09	.08	.32	.11
JAN 72	.11	.05	.004	.002	.04	.02	.03	.01	.06	.004	.46	0	.08	.10	.78	.19
\bar{x}	.12	.08	.007	.001	.03	.02	.02	.03	.04	.006	.14	.007	.09	.10		
Hi	.14	.20	.01	.002	.04	.03	.06	.06	.07	.02	.46	.02	.18	.19		
Lo	.01	0	.004	0	0	.01	0	.01	.01	---	0	0	0	0		

d = dissolved s = suspended

Table VIII. (continued)

BQD 6

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.12	.08	.04	.001	.02	.03	.02	.008	.02	0	.15	.04	.49	.15	.85	.30
MAY 71	.04	.17	.01	.002	0	.03	.04	.06	.04	.005	0	.01	.44	.34	.56	.61
JUN 71	.10	.09	.006	.001	.04	.03	.04	.06	.06	.008	.15	.02	.10	.64	.49	.86
JUL 71	.02	.03	.03	0	0	.02	.08	0	.01	.001	.20	.06	.42	.29	.76	.40
AUG 71	.06	.03	.01	0	.04	.02	0	.01	.02	.005	.05	0	.24	.02	.42	.09
SEP 71	.02	.04	.02	0	.02	.04	0	.02	.02	0	.05	0	.14	.23	.27	.33
OCT 71	.37	.67	.005	0	.03	.09	---	---	.03	.004	.08	0	.21	.50	.73	1.3
NOV 71	.05	.004	.02	.001	.04	.01	---	---	.05	0	.18	0	.20	.02	.54	.04
JAN 71	.05	.01	.001	.001	.03	.007	.04	.002	.03	.003	.03	0	.11	.05	.29	.07
\bar{x}	.9	.12	.02	.001	.02	.03	.02	.02	.03	.003	.09	.01	.26	.25		
Hi	.37	.67	.04	.002	.04	.09	.08	.06	.06	.008	.20	.06	.48	.64		
Lo	.02	.004	.001	0	0	.007	0	0	.01	0	0	0	.10	.02		

d = dissolved s = suspended

Table VIII. (continued)

BQD 9

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.09	.06	.008	.001	.02	.02	.02	.03	.02	.008	.16	.07	.04	.48	.36	.67
MAY 71	.10	.03	.006	.001	.02	.02	0	.03	.07	.005	.05	.03	.14	.34	.38	.45
JUN 71	.14	.12	.02	.002	.03	.03	.04	.06	.03	.008	.13	.01	.21	1.3	.59	1.5
JUL 71	.02	.03	.03	0	0	.02	.08	0	.01	.001	.20	.06	.42	.29	.76	.40
AUG 71	.10	.03	.01	0	.03	.02	0	.005	.04	.007	.09	0	.84	.03	1.1	.09
SEP 71	.01	.01	.03	0	.03	.03	0	.04	.02	.003	.09	0	.77	.85	.95	.93
OCT 71	.03	.21	.009	0	.04	.09	---	---	.04	.004	.05	0	.13	2.5	.30	2.8
NOV 71	.28	.01	.01	.001	.05	.02	---	---	.22	.02	.29	0	.25	.16	1.1	.21
JAN 72	.53	.04	.05	.001	.02	.01	.36	.005	.04	0	.03	.01	.39	.15	1.4	.22
\bar{x}	.14	.06	.02	.001		.03	.07	.02	.04	.006	.12	.02	.35	.70		
HI	.53	.21	.05	.002		.09	.36	.06	.23	.02	.29	.07	.84	2.5		
Lo	.01	.01	.006	0		.01	0	0	.01	0	.05	0	.04	.03		

d = dissolved s = suspended

Table VIII. (Continued)

CPB

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Σd</u>	<u>Σs</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.07	.16	.004	.001	.01	.03	0	.01	.01	.008	.10	.05	.28	.34	.47	.61
MAY 71	.03	.06	.006	0	0	.03	.04	.13	.05	0	.10	.03	.10	1.6	.32	1.8
JUN 71	.03	.18	.008	.001	0	.02	.03	.04	.06	.01	.16	.04	.02	1.8	.81	2.1
JUL 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
AUG 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
SEP 71	.04	.08	.04	.004	.02	.02	.01	.009	.03	.002	.05	.002	.11	.42	.30	.52
OCT 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
NOV 71	.18	.05	.01	.001	.02	.02	---	---	.16	.03	0	0	.10	1.7	.47	1.8
JAN 72	.12	.03	.002	.002	.07	.02	.07	.01	.02	.009	.02	0	.18	2.0	.48	2.1
\bar{x}	.08	.09	.01	.002	.02	.02	.03	.03	.06	.01	.07	.02	.14	1.3		
Hi	.18	.18	.04	.004	.07	.03	.07	.13	.16	.03	.16	.05	.28	1.8		
Lo	.03	.03	.002	0	0	.02	0	.009	.01	0	0	0	.02	.35		

d = dissolved s = suspended

Table VIII, (Continued)

DPF - A

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Σd</u>	<u>Σs</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.13	.12	.004	.002	.003	.01	.04	0	.03	.006	.15	.04	.04	.29	.42	.47
MAY 71	.02	.20	.004	0	.04	.04	.02	.05	.05	0	.03	0	.08	.26	.25	.55
JUN 71	.14	.26	.006	.001	.03	.01	.04	.04	.04	.006	.03	.03	.04	.21	.32	.56
JUL 71	.01	.04	.02	0	0	.01	.05	0	.007	.001	.06	.10	.04	.15	.19	.21
AUG 71	.24	.02	.003	0	.02	.01	0	.006	.02	.003	.03	.002	.10	.005	.41	.05
SEP 71	.18	.04	.006	0	.01	.01	0	0	.05	0	.05	0	.03	.18	.33	.23
OCT 71	.03	.03	.002	0	.02	.04	---	---	.02	.008	.04	0	.09	.25	.20	.33
NOV 71	.08	.01	.009	.006	.03	.02	---	---	.23	.02	.09	0	.07	.06	.51	.12
JAN 72	.08	.01	.007	.002	.03	.01	.05	.002	.05	.02	0	.006	.11	.08	.33	.13
\bar{x}	.10	.08	.007	.001	.02	.02	.03	.01	.05	.007	.05	.02	.07	.17		
Hi	.24	.26	.02	.006	.04	.04	.05	.05	.23	.02	.15	.10	.11	.29		
Lo	.01	.01	.002	0	0	.01	0	0	.007	0	0	0	.04	.005		

d = dissolved s = suspended

Table VIII. (Continued)

DPF - B

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Ed	Es
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.04	.06	.006	0	.06	.02	.02	.005	.02	0	.10	.10	.04	.15	.29	.33
MAY 71	.06	.18	0	0	.04	.18	0	.02	.04	0	0	.04	.20	3.3	.34	3.7
JUN 71	.08	.08	.004	.01	.02	.06	.05	.03	.03	.005	.06	.03	.11	.62	.35	.83
JUL 71	.18	.004	.03	.01	0	.01	.06	0	.003	.001	.11	.16	.02	.19	.40	.38
AUG 71	.07	.08	.008	0	.02	.03	0	.007	.30	.007	.03	.009	.22	.02	.39	.15
SEP 71	.01	.02	.02	0	.03	.04	0	.007	.04	.004	.05	0	.07	.21	.22	.28
OCT 71	.08	.45	.005	0	.05	.08	---	---	.04	0	.04	.007	.05	.20	.27	.74
NOV 71	.07	.01	.008	.002	.03	.02	---	---	.10	.02	.07	.006	.09	.08	.37	.14
JAN 72	.24	.01	.004	.002	.10	.03	.03	0	.08	.01	0	.006	.14	.02	.59	.08
\bar{x}	.09	.10	.009	.003	.04	.05	.02	.01	.04	.005	.05	.04	.10	.53		
Hi	.18	.45	.03	.01	.10	.18	.06	.03	.10	.02	.10	.16	.22	3.3		
Lo	.01	.004	0	0	0	.01	0	0	.003	0	0	0	.02	.02		

d = dissolved s = suspended

Table VIII. (Continued)

DPF - C

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.02	.09	.004	0	.02	.02	0	0	.02	0	.12	.04	.06	.18	.24	.27
MAY 71	.01	.09	.008	.001	0	.05	.03	.04	0	.005	0	.01	.03	.27	.08	.47
JUN 71	.01	.02	.004	0	.03	.03	0	.06	.04	.007	.10	.02	.04	.27	.22	.41
JUL 71	.18	.004	.03	.01	0	.01	.06	0	0	.001	.11	.16	.02	.19	.40	.38
AUG 71	.03	.08	.004	0	.03	.02	0	.005	0	.003	.02	.006	.02	.02	.10	.13
SEP 71	.14	.10	.003	0	.08	.01	0	0	.01	.001	.01	.006	.04	.04	.28	.16
OCT 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
NOV 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
JAN 72	.07	.03	.006	.002	.13	.02	.03	.001	.04	.01	.04	0	.06	.08	.32	.14
\bar{x}	.06	.06	.01	.002	.04	.02	.02	.01	.02	.004	.06	.03	.04	.14		
Hi	.18	.10	.03	.01	.13	.05	.06	.06	.04	.01	.11	.16	.06	.27		
Lo	.01	.004	.003	0	0	.01	0	0	0	.001	0	0	.02	.02		

d = dissolved s = suspended

Table VIII. (Continued)

DPQ - H

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.01	.09	.01	.001	.01	.04	.02	.15	.04	.006	.14	.10	.12	.45	.35	.85
MAY 71	.08	.25	.01	.001	0	.06	.04	.34	.02	0	.10	.18	.20	.19	.42	.82
JUN 71	.03	.12	.004	.001	.05	.14	.03	.18	.04	.008	.07	.09	.04	3.4	.26	3.9
JUL 71	.10	.08	0	.02	.03	.13	.08	0	0	.001	.10	.16	.09	.98	.31	1.4
AUG 71	.08	.46	.009	0	.01	.16	.08	.27	.02	.007	.03	.07	.13	.06	.36	1.0
SEP 71	.04	.01	.003	0	.01	.01	0	.004	.02	.002	.02	0	.11	.38	.20	.41
OCT 71	.13	.21	.002	0	.02	.12	---	---	.03	.004	.02	0	.05	.60	.25	.93
NOV 71	.05	.03	.01	0	.04	.02	---	---	.13	.02	.08	.01	.03	.14	.34	.22
JAN 72	.05	.08	.02	.002	.11	.08	.25	.04	.08	.01	.02	.03	.27	.36	.80	.62
\bar{x}	.05	.15	.008	.003	.03	.08	.07	.14	.04	.006	.06	.07	.11	.73		
Hi	.13	.46	.02	.02	.11	.16	.25	.34	.13	.01	.14	.18	.27	3.4		
Lo	.01	.01	0	0	0	.01	0	0	0	0	.02	0	.03	.06		

d = dissolved s = suspended

Table VIII. (Continued)

DPQ - 0

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.03	.05	.006	0	.01	.04	.02	.06	.02	0	.08	.05	.04	.45	.21	.66
MAY 71	.05	.39	.02	0	0	.05	.04	.12	.04	0	.08	.07	.20	.19	.42	.82
JUN 71	.03	.08	.006	0	.02	.09	0	.09	.05	.004	.05	.05	.06	2.2	.21	2.5
JUL 71	.02	.05	.02	.02	0	.02	.06	0	0	.001	.12	.06	0	1.8	.22	2.0
AUG 71	.008	.02	.006	0	.02	.02	0	.02	.02	0	.02	.02	.04	.02	.11	.10
SEP 71	.03	.01	.02	0	.01	.03	.03	.03	.03	.002	.03	.002	.04	.07	.19	.14
OCT 71	.09	.05	.002	0	.04	.05	---	---	.02	.004	.04	0	.05	.60	.24	.71
NOV 71	.04	.05	.009	.001	.03	.13	---	---	.09	.02	.08	.06	.06	.40	.31	.66
JAN 72	.03	.05	.006	.002	.04	.11	.12	.02	.07	.01	.02	.03	.20	.44	.49	.66
\bar{x}	.04	.08	.01	.003	.02	.06	.04	.05	.04	.005	.06	.04	.03	.69		
H1	.09	.39	.02	.02	.04	.11	.12	.12	.09	.02	.12	.07	.20	2.2		
Lo	.008	.01	.002	0	0	.02	0	0	0	0	.02	0	0	.02		

d = dissolved s = suspended

Table VIII. (Continued)

ETE SI

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.05	.05	.008	0	.02	.03	.02	0	.04	.006	.08	.03	.36	.29	.58	.41
MAY 71	.02	.05	.006	.003	.01	0	.06	0	.03	.01	.05	0	.22	.50	.39	.56
JUN 71	.02	.16	.008	.002	.02	.03	0	.08	.04	.01	.04	.06	.40	.69	.53	1.0
JUL 71	.08	.08	.05	.03	0	.02	.02	0	0	.004	.12	.09	.24	.50	.51	.76
AUG 71	.01	.04	.006	0	.01	.02	0	.005	.03	.007	.06	.008	.60	.02	.72	.10
SEP 71	.04	.21	.004	.002	.03	.03	0	.03	.09	.003	.06	.04	3.0	.68	3.2	1.0
OCT 71	.27	.13	.006	0	.02	.18	---	---	.05	.006	.05	.05	.10	1.0	.50	1.5
NOV 71	.27	.02	.02	.001	.05	.04	---	---	.21	.01	.13	.008	.08	.17	.76	.25
JAN 72	.31	.02	.01	.002	.05	.02	.08	.002	.11	.01	.03	.008	.48	.20	1.1	.26
\bar{X}	.12	.07	.01	.004	.02	.04	.03	.02	.07	.01	.07	.03	.60	.45		
Hi	.31	.21	.05	.03	.05	.18	.08	.08	.21	.04	.13	.09	3.0	1.0		
Lo	.01	.02	.004	0	0	0	0	0	0	.003	.03	0	.08	.02		

d = dissolved s = suspended

Table VIII. (Continued)

ETE SJ

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Σd</u>	<u>Σs</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.05	.25	.01	.003	.02	.02	.02	.01	.04	.01	.17	.03	.08	.07	.39	.39
MAY 71	.05	.03	.008	.003	0	.004	.02	.05	.03	.02	.05	.05	.04	.16	.20	.32
JUN 71	.05	.03	.004	.001	.03	.03	.03	.03	.07	.007	.12	.02	.02	.26	.33	.38
JUL 71	.13	.04	.04	.03	0	.006	.03	0	.02	.001	.03	.144	0	.11	.25	.33
AUG 71	.02	.04	.003	0	.01	.006	0	.008	.01	.007	.01	.004	.02	.06	.07	.13
SEP 71	.01	.03	.007	.04	.01	.05	0	.03	.15	.01	.01	.01	.11	.53	.30	.70
OCT 71	.04	.12	.001	.001	.01	.07	---	---	.03	.005	.01	0	.03	.95	.12	1.1
NOV 71	.03	.01	.01	.001	.02	.01	---	---	.24	.02	.07	.009	.03	.05	.18	.10
JAN 72	.04	.007	.01	.002	.05	.02	.05	.001	.10	.01	.02	0	.14	.08	.41	.12
\bar{X}	.05	.06	.01	.009	.02	.02	.02	.02	.08	.01	.05	.03	.05	.25		
Hi	.13	.25	.04	.04	.05	.07	.05	.05	.24	.02	.17	.14	.14	.95		
Lo	.01	.007	.001	0	0	.004	0	0	.01	.001	.01	0	0	.05		

d = dissolved s = suspended

Table VIII. (Continued)

ETE SK

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.48	.43	0	.002	.008	.03	0	0	.03	.008	.10	.05	.33	.20	.94	.72
MAY 71	.03	.09	.008	.003	.02	.03	0	.05	.05	.005	.05	.04	.12	1.1	.28	1.4
JUN 71	.32	.07	.004	.001	0	.05	.05	.02	.06	.009	.11	.03	.04	.46	.58	.64
JUL 71	.03	.27	.03	.28	0	.02	.06	00	.01	.002	.10	.19	0	.34	.23	1.1
AUG 71	.03	.04	.006	0	.01	.008	0	.007	.03	0	.01	.01	.06	.06	.15	.13
SEP 71	.06	.04	0	.003	.03	.02	0	.04	.04	.01	.03	.008	.03	.26	.19	.38
OCT 71	.29	2.0	.002	.001	.02	.11	---	---	.06	.008	.03	.02	.03	1.9	.43	3.9
NOV 71	.03	.01	.01	.001	.03	.01	---	---	.28	0	.07	.004	.06	.06	.48	.09
JAN 72	.28	.03	.007	.002	.03	.007	.08	.002	.09	.003	.02	.02	.24	.71	.75	.77
\bar{X}	.15	.34	.007	.03	.02	.03	.02	.02	.07	.005	.06	.04	.10	.56		
Hi	.48	2.0	.03	.28	.03	.11	.08	.05	.28	.01	.11	.19	.33	1.8		
Lo	.03	.03	0	0	0	.007	0	0	.01	0	.01	.005	0	.06		

d = dissolved s = suspended

Table VIII. (Continued)

ETU 60.10

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.01	.09	0	.002	0	.03	.36	.07	.03	.006	.03	.10	.20	.19	.63	.50
MAY 71	.08	.50	.01	0	.02	.10	0	.96	.05	.02	.05	.44	.36	.62	.58	2.6
JUN 71	.06	.10	.004	.001	0	.03	.02	.13	.02	.006	.10	.11	.08	.27	.29	.65
JUL 71	.02	.08	.03	.02	0	.04	0	0	0	.001	.05	.32	.06	.09	.16	.55
AUG 71	.10	.02	0	0	.004	.01	0	.005	.006	.003	.03	.003	.08	.01	.22	.05
SEP 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
OCT 71	.07	.09	.01	0	.009	.16	---	---	.01	.005	.04	.004	.09	.32	.23	.58
NOV 71	.04	.06	0	0	.01	.05	---	---	.04	.009	.03	0	.02	.29	.14	.41
JAN 71	.02	.09	.006	.001	.02	.08	.07	.03	0	.01	.02	.03	.20	.32	.34	.56
\bar{X}	.05	.13	1007	.003	.008	.06	.06	.20	.02	.009	.04	.12	.13	.26		
H1	.10	.50	.03	.02	.02	.16	.36	.06	.05	.02	.10	.44	.36	.62		
Lo	.02	.02	0	0	0	.01	0	0	0	.001	.02	0	.02	.01		

d = dissolved s = suspended

Table VIII. (Continued)

NDD

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.01	.50	.006	.003	.03	.02	0	.13	.02	0	.15	.03	.04	.32	.25	1.0
MAY 71	.05	.13	.01	.002	0	.005	.08	.79	.05	.009	.07	.05	.12	1.2	.37	2.2
JUN 71	.10	.06	.004	.001	.02	.03	.03	.18	.02	.004	.09	.02	.06	.43	.31	.73
JUL 71	---	---	---	---	---	---	---	---	---	---	---	---	---	---		
AUG 71	.40	.02	.003	0	.02	.009	0	.03	.009	.004	.04	.003	.06	.02	.53	.09
SEP 71	.009	.02	.006	.001	.01	.01	.02	.02	.03	.003	.02	.004	.11	.17	.21	.23
OCT 71	.14	.04	.002	0	.03	.11	---	---	.006	.002	.06	0	.03	.70	.27	.85
NOV 71	.05	.004	.006	0	.02	.01	---	---	.04	.009	0	.006	.05	.04	.16	.07
JAN 72	.06	.02	.004	.001	.16	.05	.06	.007	.05	.02	.02	.06	.27	.38	.63	.55
\bar{X}	.10	.10	.005	.001	.04	.03	.03	.19	.03	.006	.06	.02	.09	.41		
Hi	.10	.50	.01	.003	.16	.11	.08	.78	.05	.02	.15	.07	.27	1.2		
Lo	.01	.004	.003	0	0	.005	0	.007	.005	0	0	0	.03	.02		

d = dissolved s = suspended

Table VIII. (Continued)

TSQ ABOVE

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		<u>Σd</u>	<u>Σs</u>
	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>	<u>d</u>	<u>s</u>		
APR 71	.01	.06	.01	.001	.02	.01	0	0	.02	.006	.15	.03	.04	.11	.25	.22
MAY 71	.02	.08	.004	0	0	.02	0	.02	.90	.007	.05	.01	.03	.34	.19	.47
JUN 71	.02	.10	0	.001	0	.06	.02	.10	.03	.04	.05	.06	.04	5.8	.16	6.2
JUL 71	.03	.20	.03	.02	0	.01	.02	0	.005	.001	.06	.06	0	2.3	.15	2.6
AUG 71	.36	.10	.003	0	.02	.02	0	.01	.003	.009	.02	.01	.02	.45	.43	.60
SEP 71	.02	.005	.002	.001	.006	.009	0	.004	.03	.002	.03	0	.02	.03	.11	.05
OCT 71	.09	.13	.001	0	.02	.06	---	---	.009	.01	.02	0	.01	1.2	.15	.14
NOV 71	.01	.01	.003	.003	.04	.02	---	---	.04	.06	.02	0	.02	1.6	.13	1.7
JAN 72	.07	.02	.003	.003	.11	.20	.05	.003	.03	.009	.05	.003	.06	1.7	.38	1.9
\bar{X}	.07	.09	.007	.003	.02	.004	.01	.02	.03	.02	.05	.02	.03	1.5		
Hi	.36	.20	.01	.02	.11	.20	.05	.10	.09	.06	.15	.06	.06	5.8		
LO	.01	.01	0	0	0	.01	0	0	.003	.001	.02	0	0	.03		

d = dissolved s = suspended

Table VIII. (Continued)

TSQ BELOW

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.01	.03	.006	0	.02	.01	0	0	.03	0	.17	.07	.04	.11	.27	.22
MAY 71	.005	.34	.004	.01	.02	.02	0	.02	.04	.004	.10	.03	0	.52	.17	.94
JUN 71	.03	.12	.006	.001	0	.07	.03	.07	.02	.04	0	.09	.06	6.4	.15	6.8
JUL 71	.03	.03	0	0	0	.01	.05	0	0	.001	.14	.08	0	1.4	.22	1.5
AUG 71	.13	.08	.003	0	.02	.02	0	.008	0	0	.02	.005	.04	.35	.21	.46
SEP 71	.43	.01	.005	.001	.009	.01	0	.009	.03	.001	.02	0	.02	.32	.51	.35
OCT 71	.006	.13	.001	0	.03	.12	---	---	.02	.05	.01	0	.01	1.0	.08	2.2
NOV 71	.01	.01	.006	0	.03	.02	---	---	.02	.01	.09	0	.02	1.5	.18	1.5
JAN 72	.26	.06	.005	.002	.13	.02	.08	.001	.03	.004	.04	.01	.12	.12	.43	.22
\bar{X}	.10	.09	.004	.002	.03	.03	.02	.01	.02	.007	.07	.03	.03	1.4		
Hi	.43	.34	.006	.01	.13	.12	.08	.07	.04	.04	.14	.09	.12	6.4		
Lo	.005	.01	0	0	0	.01	0	0	0	0	.01	0	0	.11		

d = dissolved s = suspended

Table VIII. (Continued)

TSQ EFF.

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71	.04	.07	.006	0	.02	.03	.22	.07	.02	0	.10	.03	.08	.69	.49	.90
MAY 71	.08	.14	0	0	.02	.06	.88	.42	0	.009	.15	.08	.20	.50	1.3	1.2
JUN 71	.05	.04	.006	.001	.09	.03	.10	.08	.02	.004	.07	.04	.64	.77	.98	.96
JUL 71	.12	110	.03	0	.28	.05	0	0	.006	.002	.06	1.1	.21	3.1	.71	4.4
AUG 71	.01	.01	.006	0	.04	.006	1.1	.006	.02	0	.05	.005	.88	0	2.1	.03
SEP 71	.03	.07	.004	.002	.03	.06	.90	.25	.02	.003	.05	.10	.21	.36	.83	.85
OCT 71	.04	.60	0	0	.03	.09	---	---	.01	.01	.03	0	.24	.28	.35	.98
NOV 71	.003	.02	.01	.001	.02	.02	---	---	.07	.02	.07	.005	.08	.12	.25	.19
JAN 72	.39	.08	.46	.003	.10	.05	.74	.02	.02	.007	.15	.02	.30	.31	2.3	.49
\bar{X}	.08	.13	.06	.001	.08	.04	.51	.12	.02	.006	.08	.15	.32	.68		
Hi	.39	.60	.46	.003	.28	.09	1.1	.42	.07	.02	.15	1.1	.88	3.1		
Lo	.003	.01	0	0	.02	.006	0	0	0	0	.03	0	.08	0		

d = dissolved s = suspended

Table VIII. (continued)

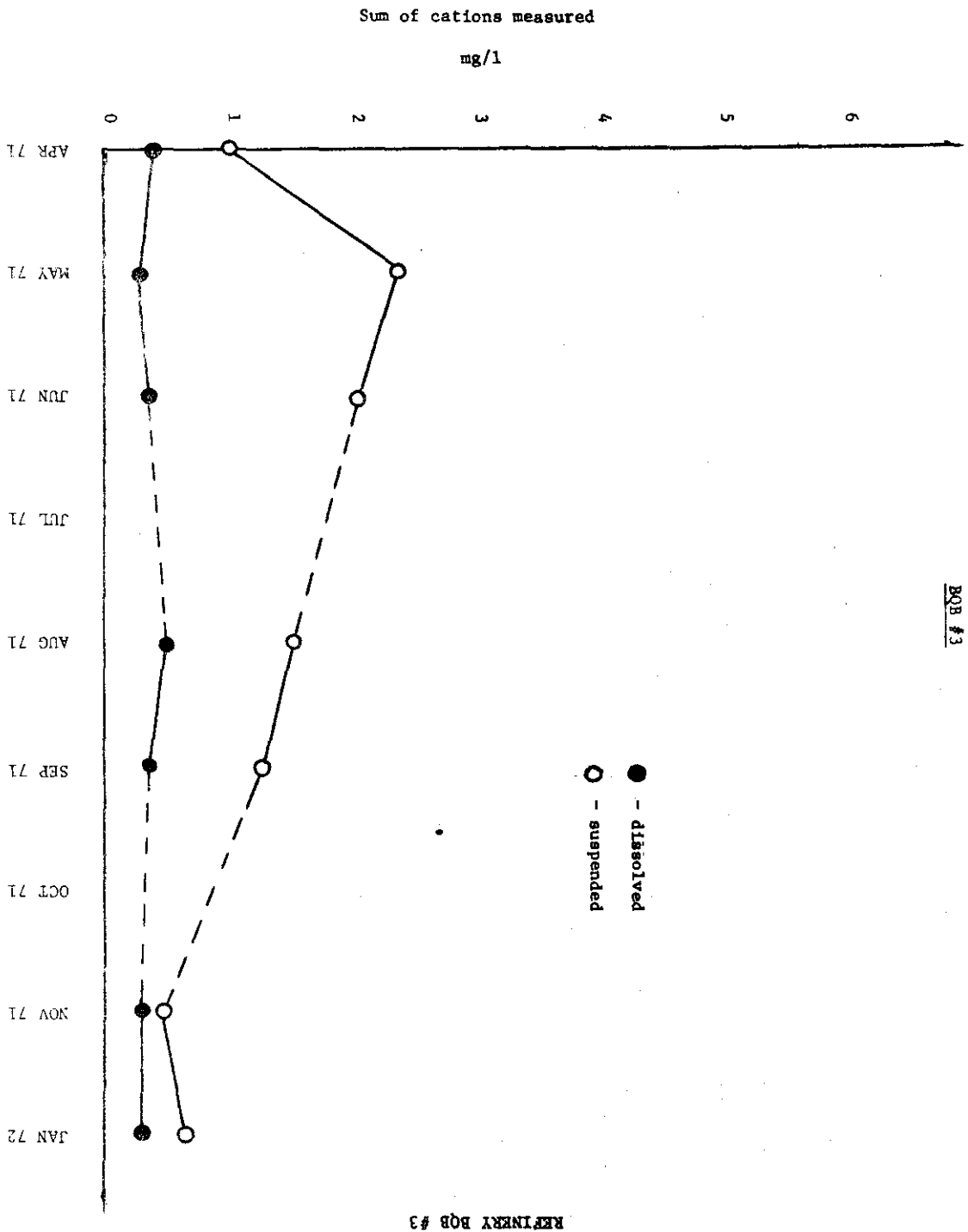
UWU

	Zn		Cd		Cu		Cr		Ni		Pb		Fe		Σd	Σs
	d	s	d	s	d	s	d	s	d	s	d	s	d	s		
APR 71																
APR 71	.37	.12	.008	0	.04	.10	.02	.008	.02	.01	.15	.05	.27	.69	.88	.98
MAY 71	.03	.47	.01	.003	.05	.19	0	.04	.03	.009	0	.32	1.2	0	1.3	1.0
JUN 71	.04	.35	.006	.001	.02	.18	0	.02	.06	.01	.06	.17	.58	1.1	.75	1.9
JUL 71	.20	.30	.04	.03	0	.02	.04	0	0	.001	.10	.26	.09	.35	.47	.96
AUG 71	.14	.22	.003	0	.02	.05	0	.008	.008	.007	.02	.01	.24	.07	.43	.37
SEP 71	.05	.01	0	.001	.01	.007	0	.01	.01	.004	.06	.02	.17	.24	.30	.29
OCT 71	.59	.40	.005	0	.04	.36	---	---	.02	.007	.03	.02	.9	3.3	1.6	4.1
NOV 71	1.9	.07	.006	0	.03	.07	---	---	.17	-	.06	.09	.21	.15	2.4	.38
JAN 72	.31	.09	0	.001	.02	.09	.05	.002	.02	.01	.05	.03	.33	.69	.78	.91
\bar{X}	.34	.22	.009	.004	.02	.12	.02	.01	.04	.006	.06	.11	.44	.73		
H1	1.9	.47	.04	.03	.05	.36	.05	.04	.17	.01	.10	.32	1.2	3.3		
Lo	.03	.01	0	0	0	.02	0	0	0	0	0	.01	.09	0		

d = dissolved s = suspended

Table VIII. (Continued)

BOB #3



REFINERY BOB #3

FIG. 28. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

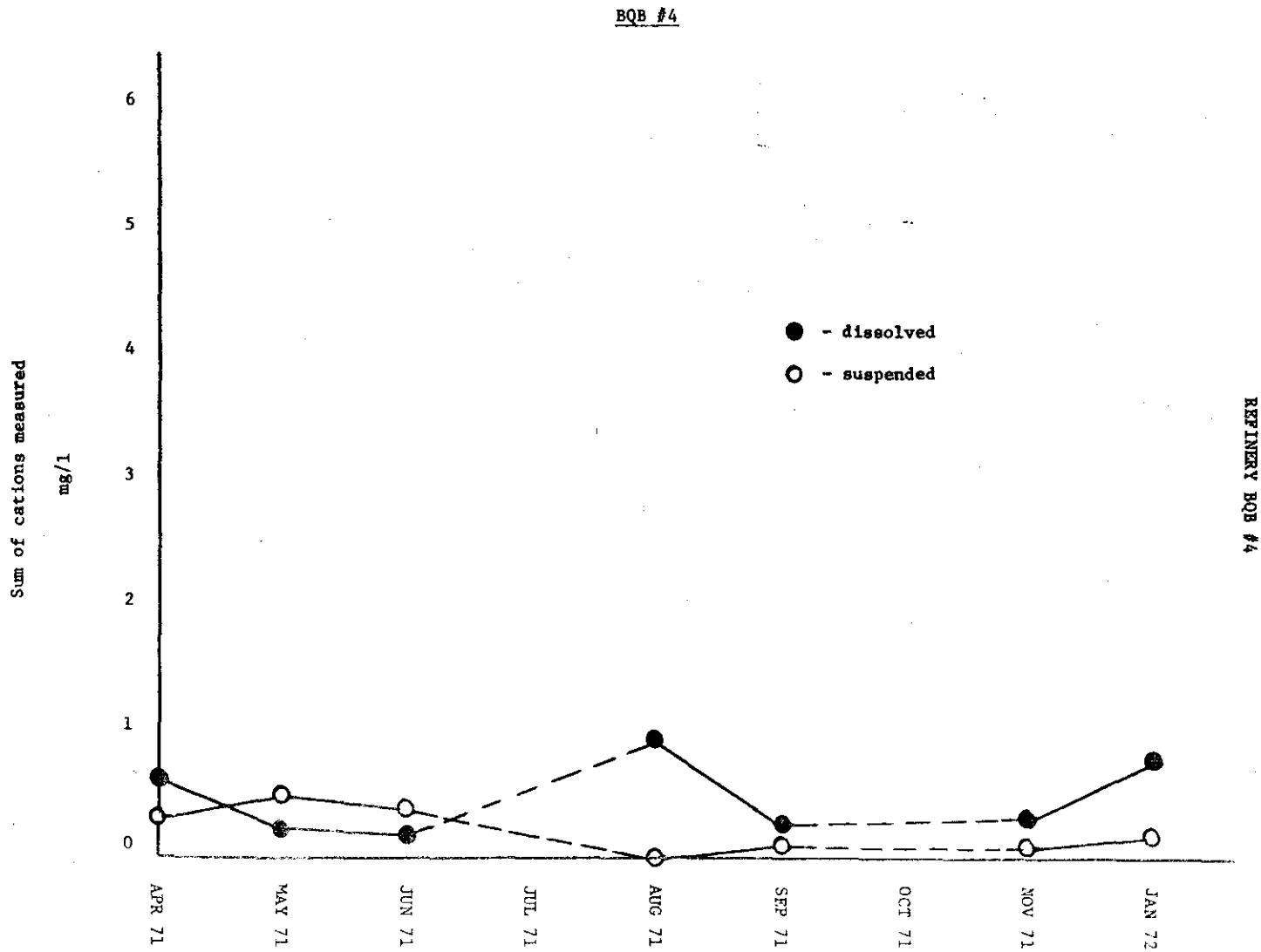


Fig. 29. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

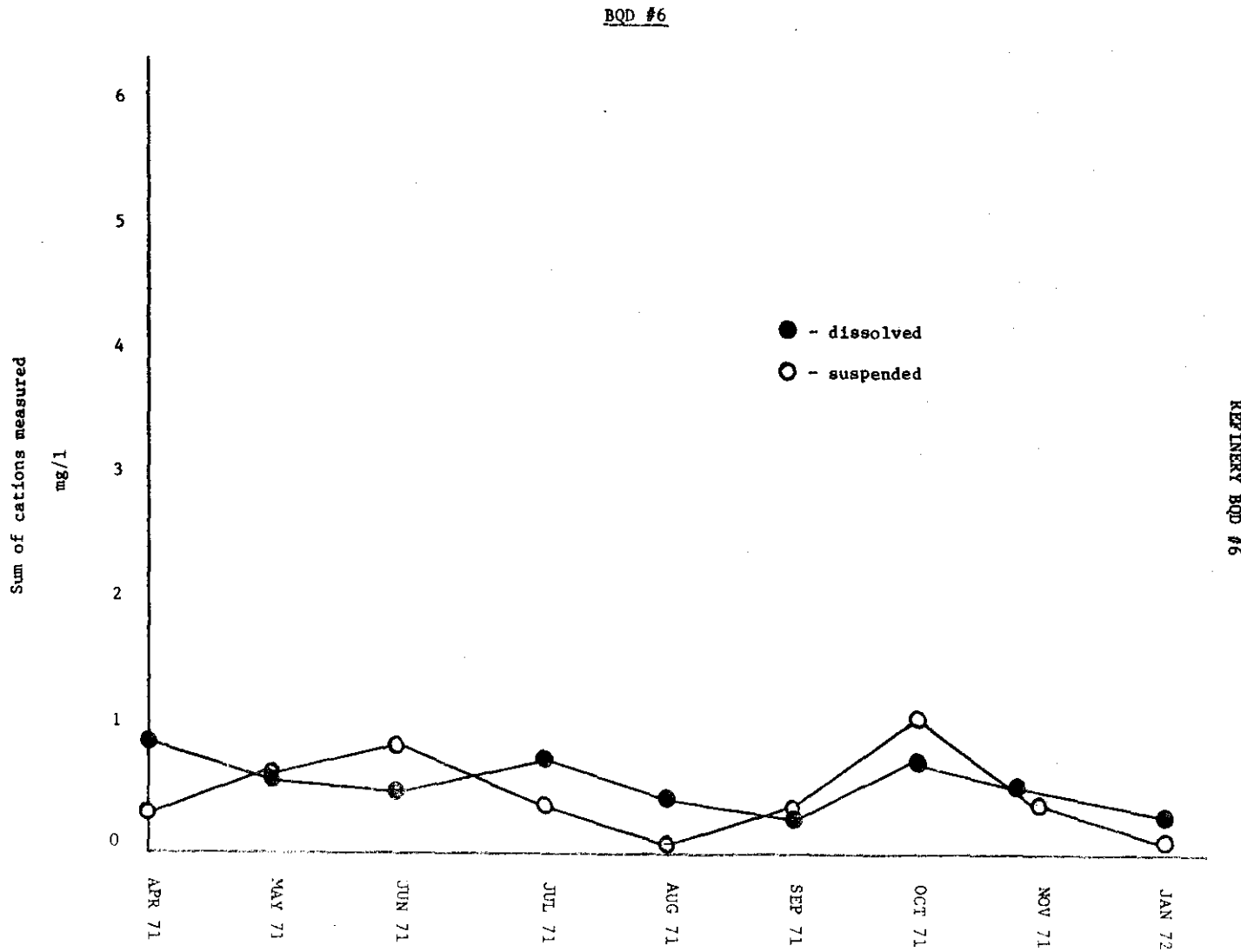


Fig. 30. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

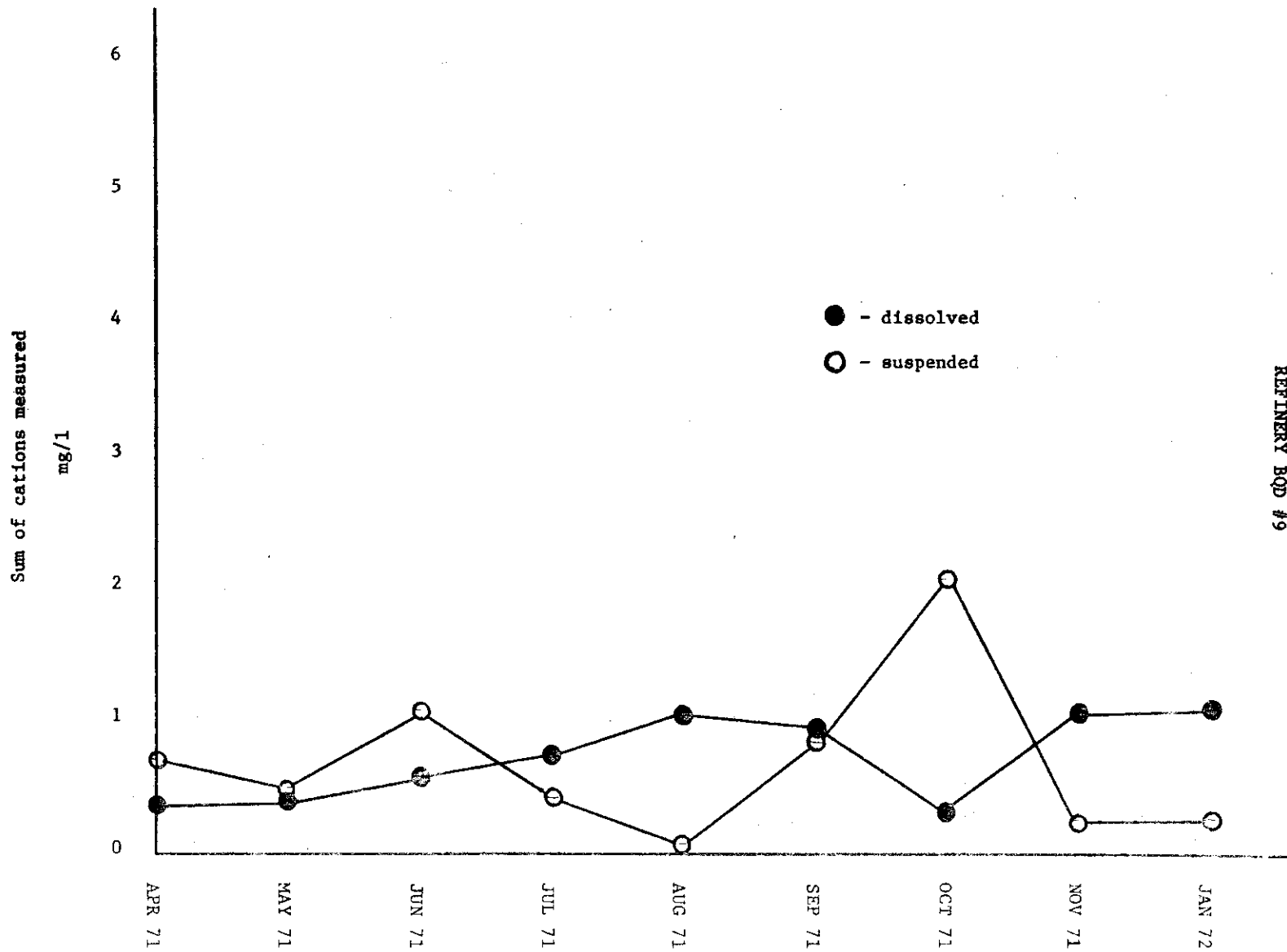


Fig. 31. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

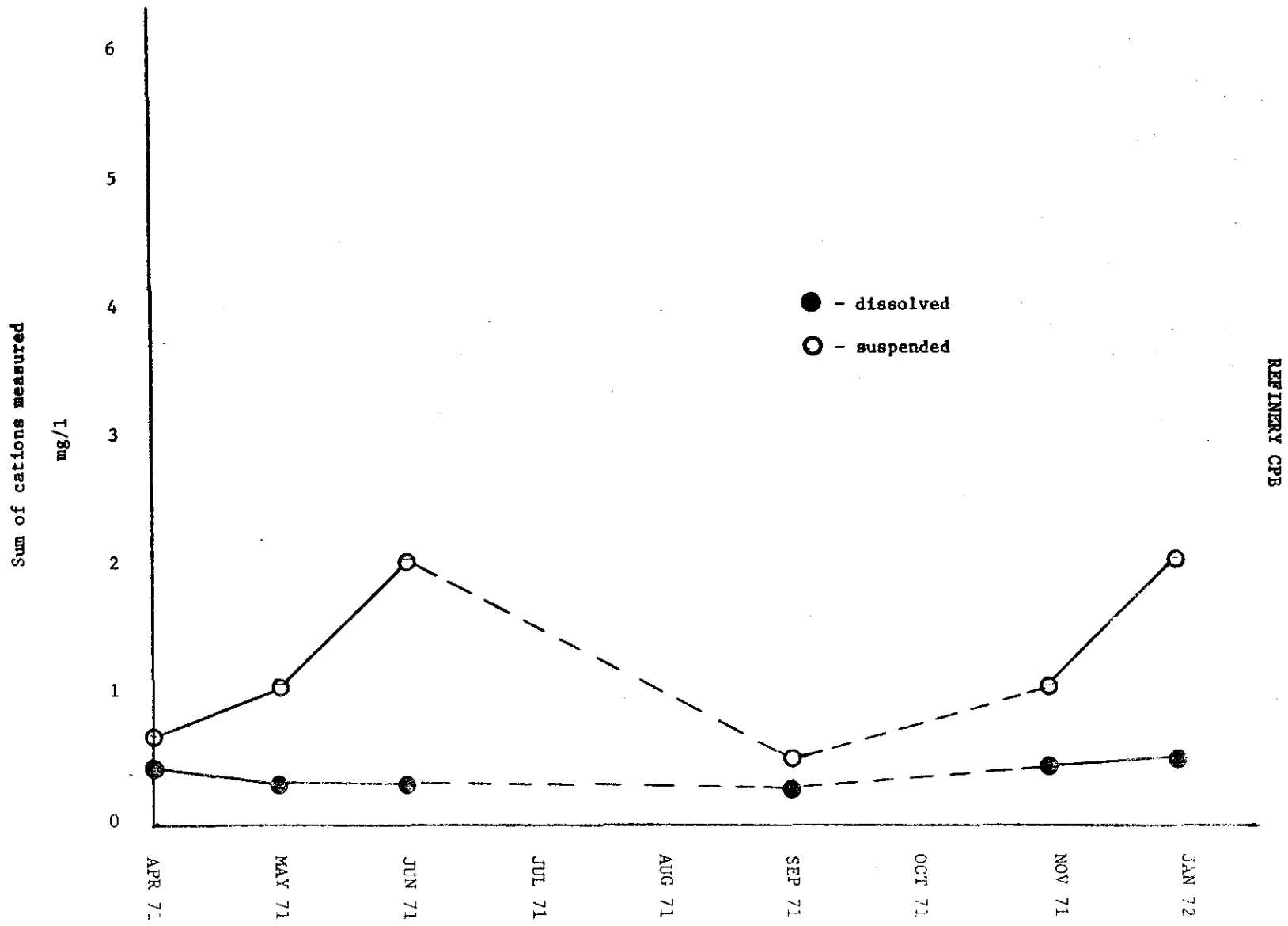


Fig. 32. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

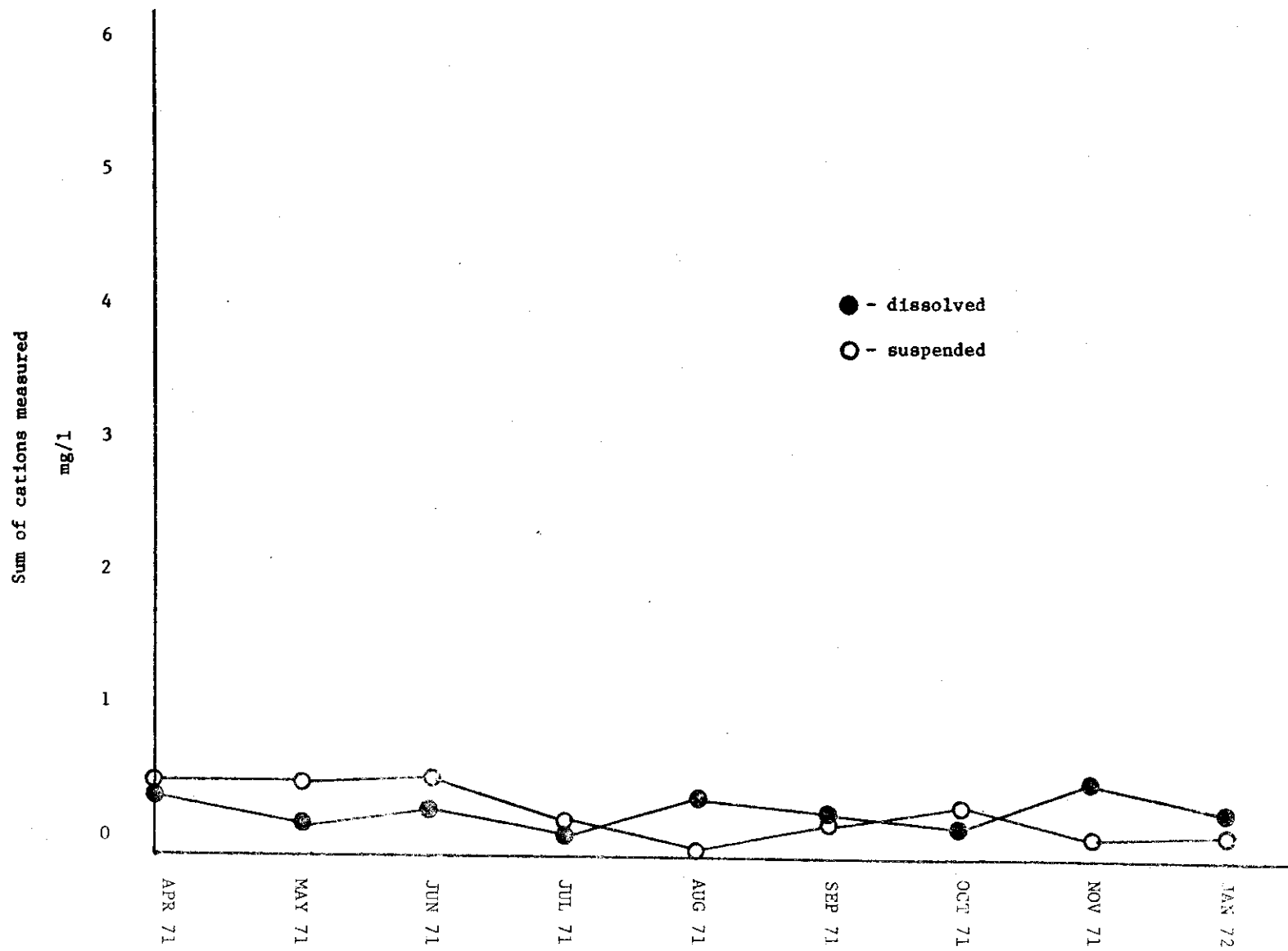


Fig. 33. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

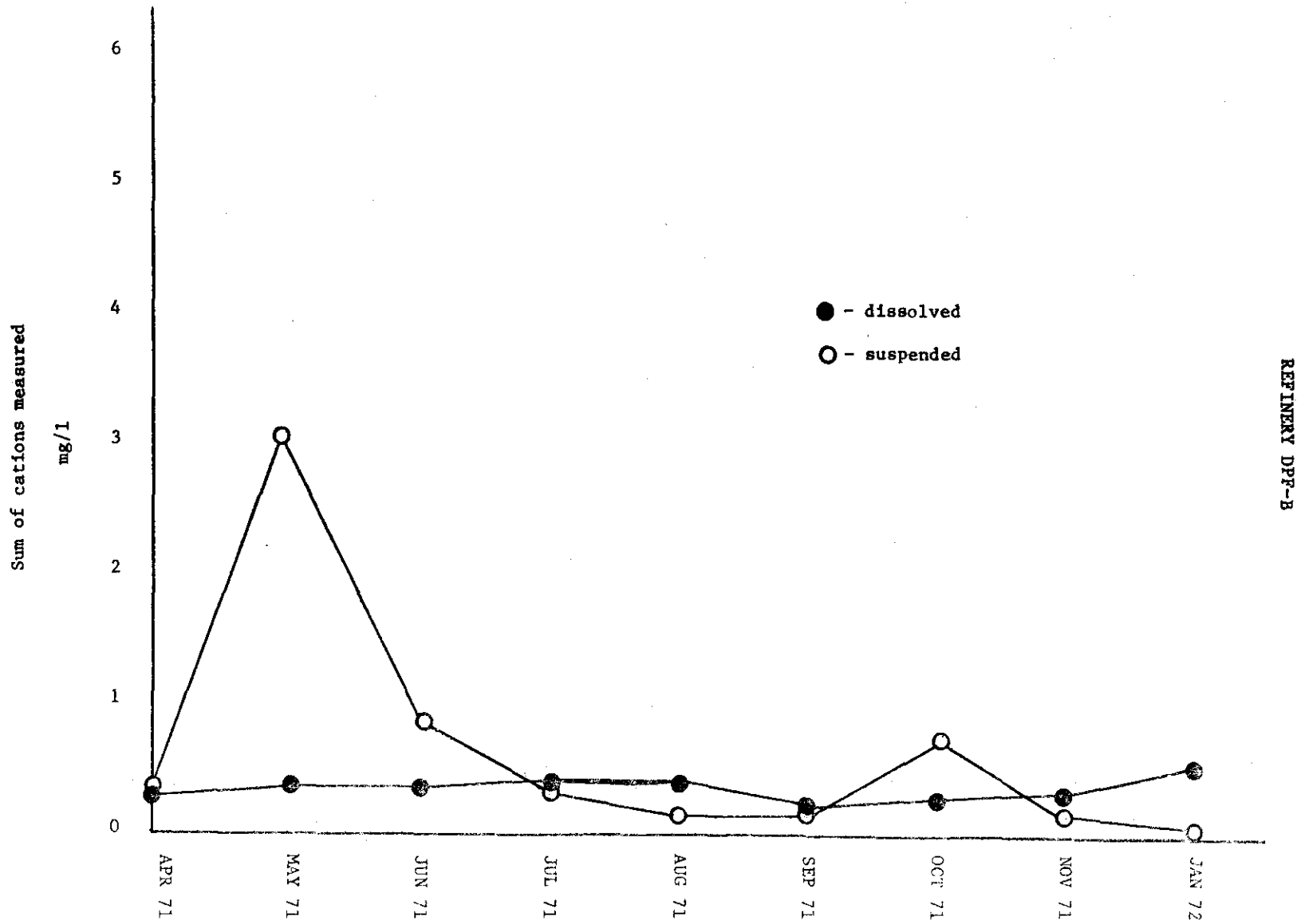


Fig. 34. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

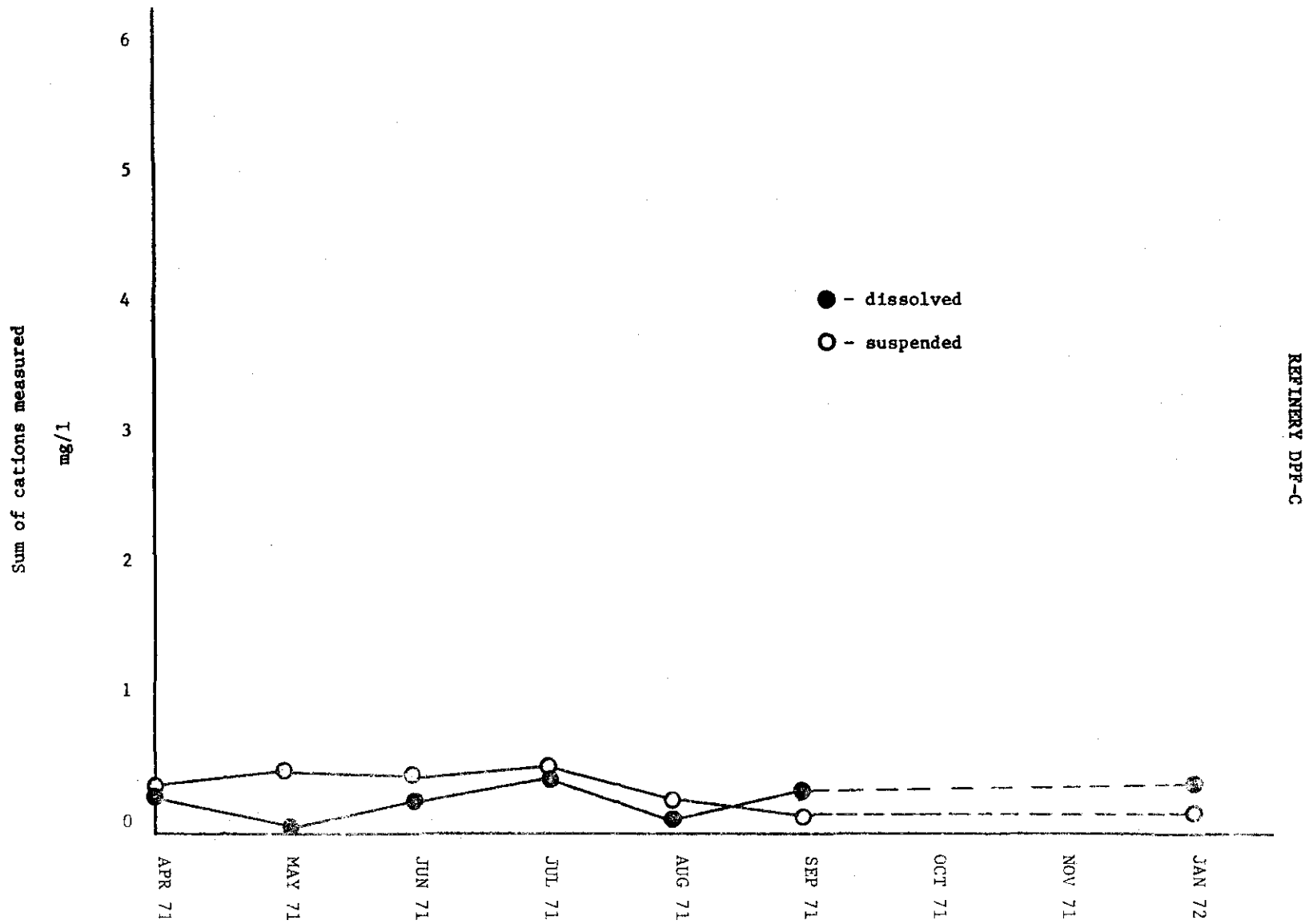
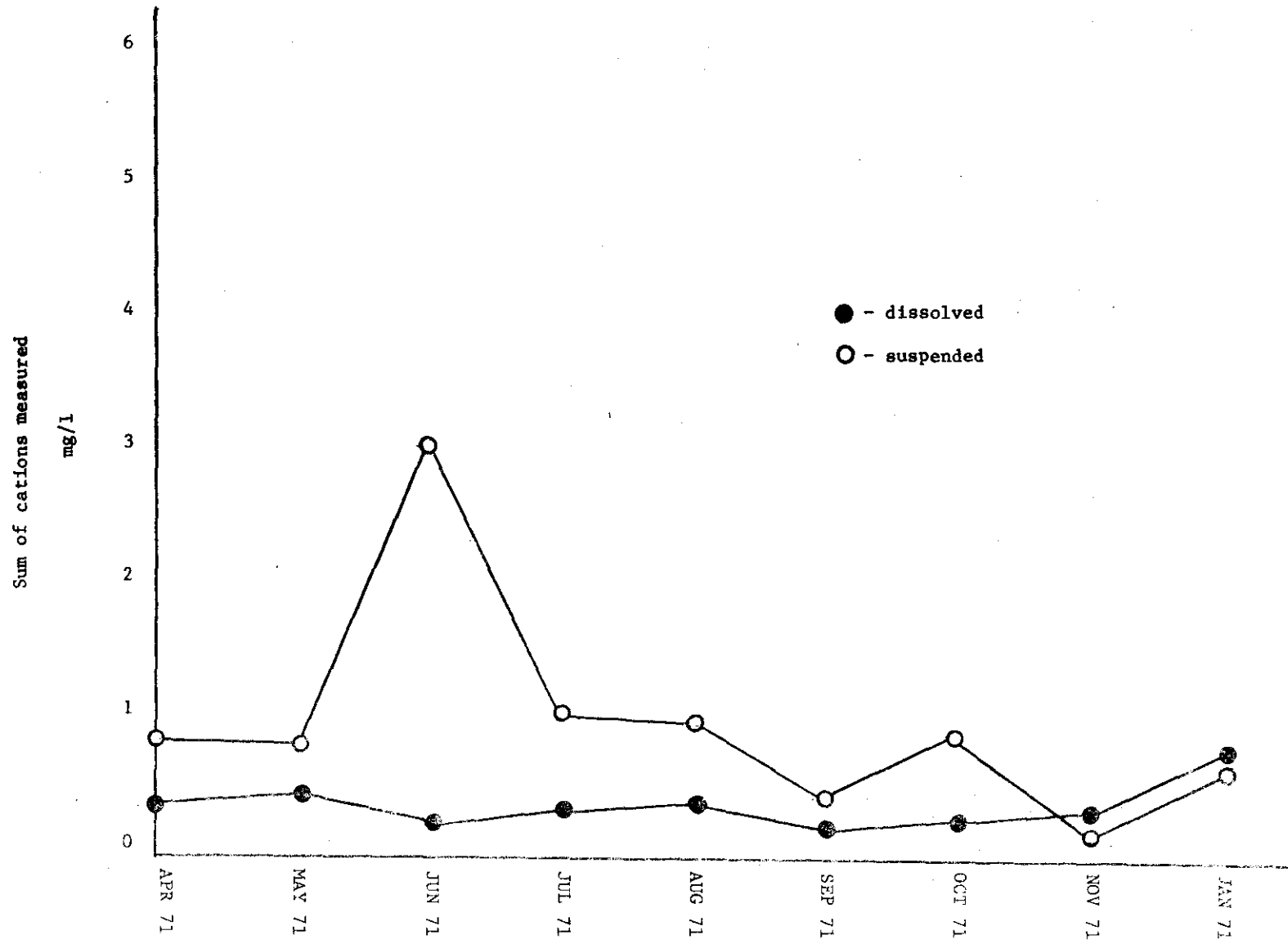


Fig. 35. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.



REFINERY DPQ-H

Fig. 36. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

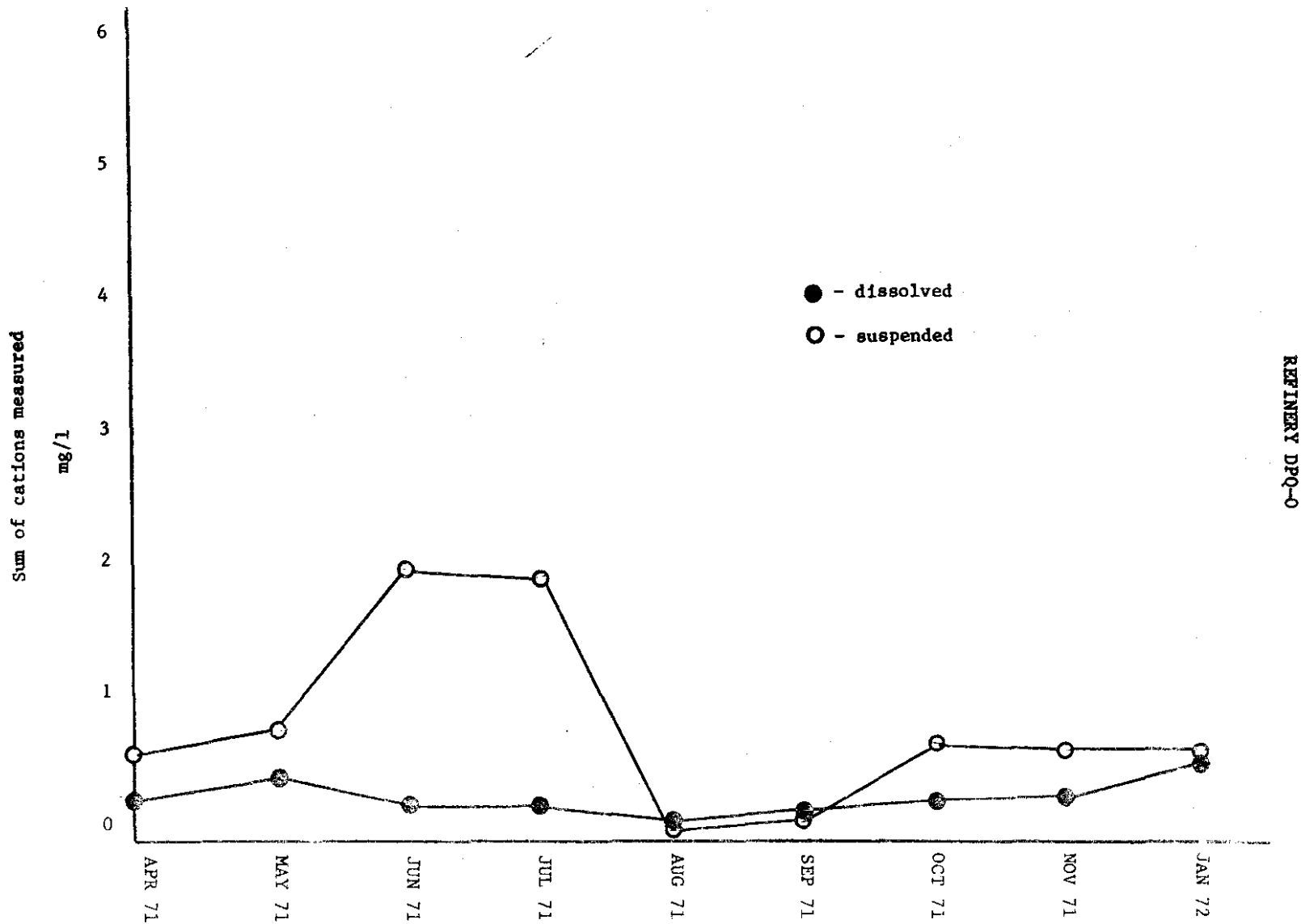


Fig. 37. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

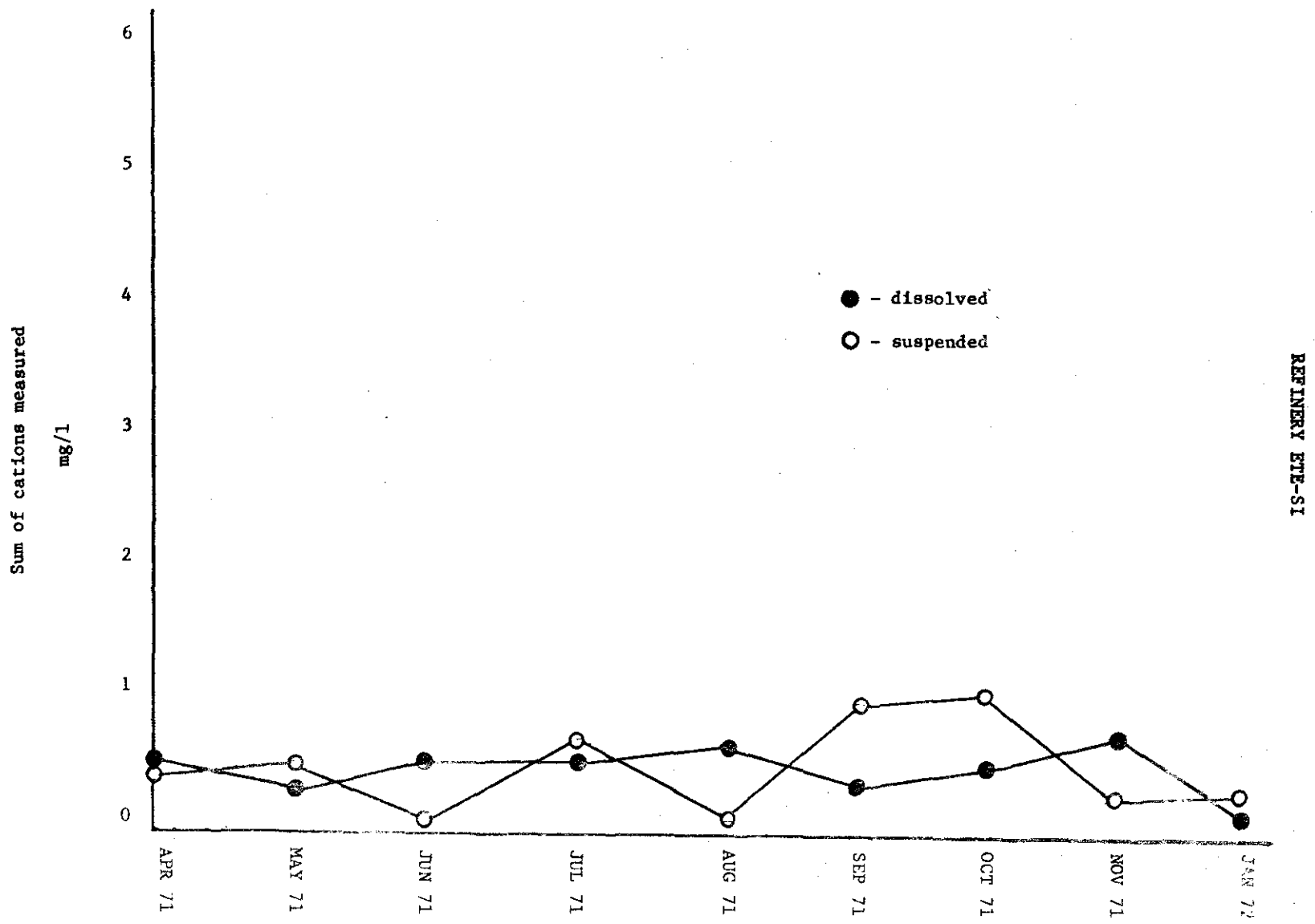


Fig. 38. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

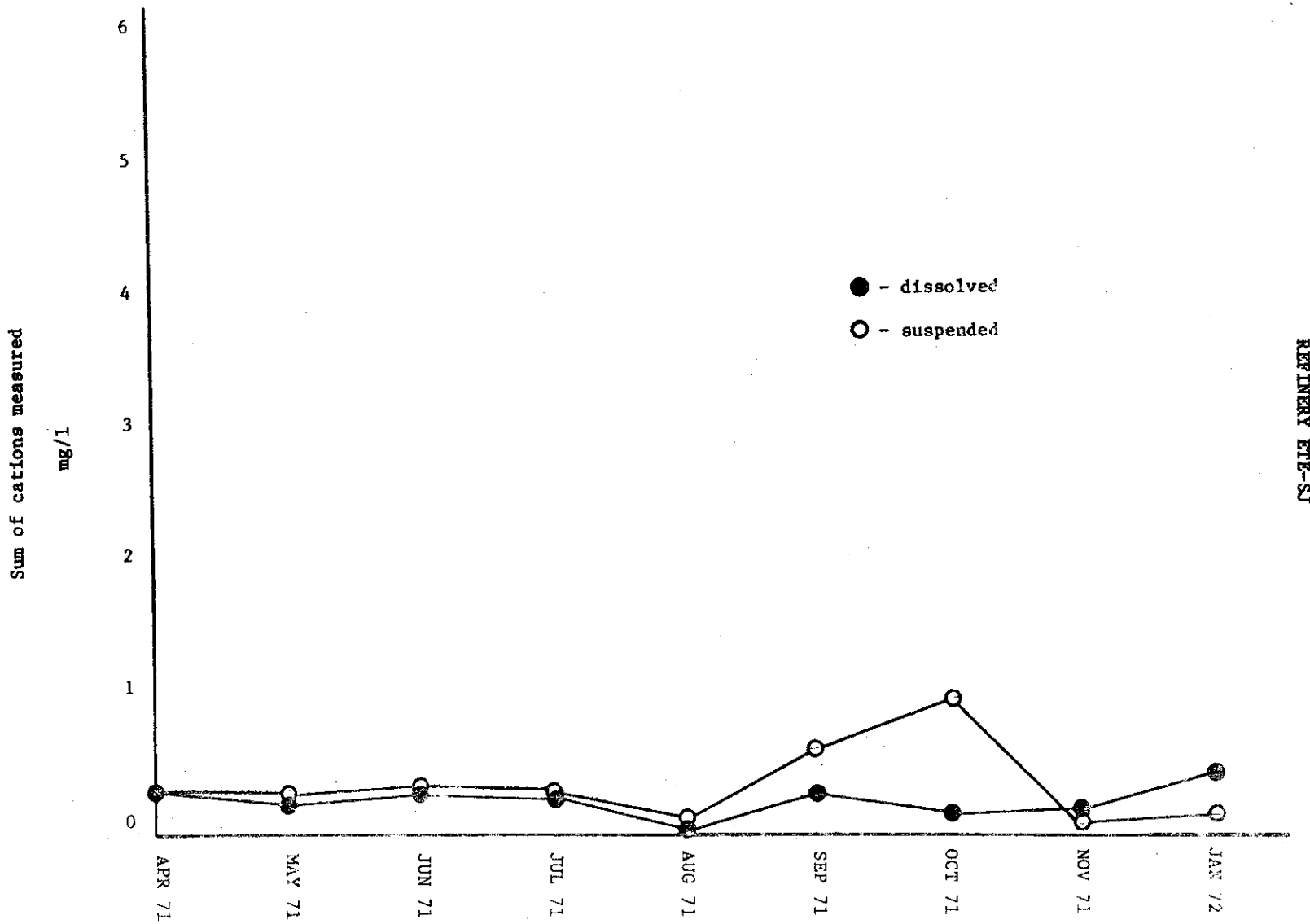


Fig. 39 Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

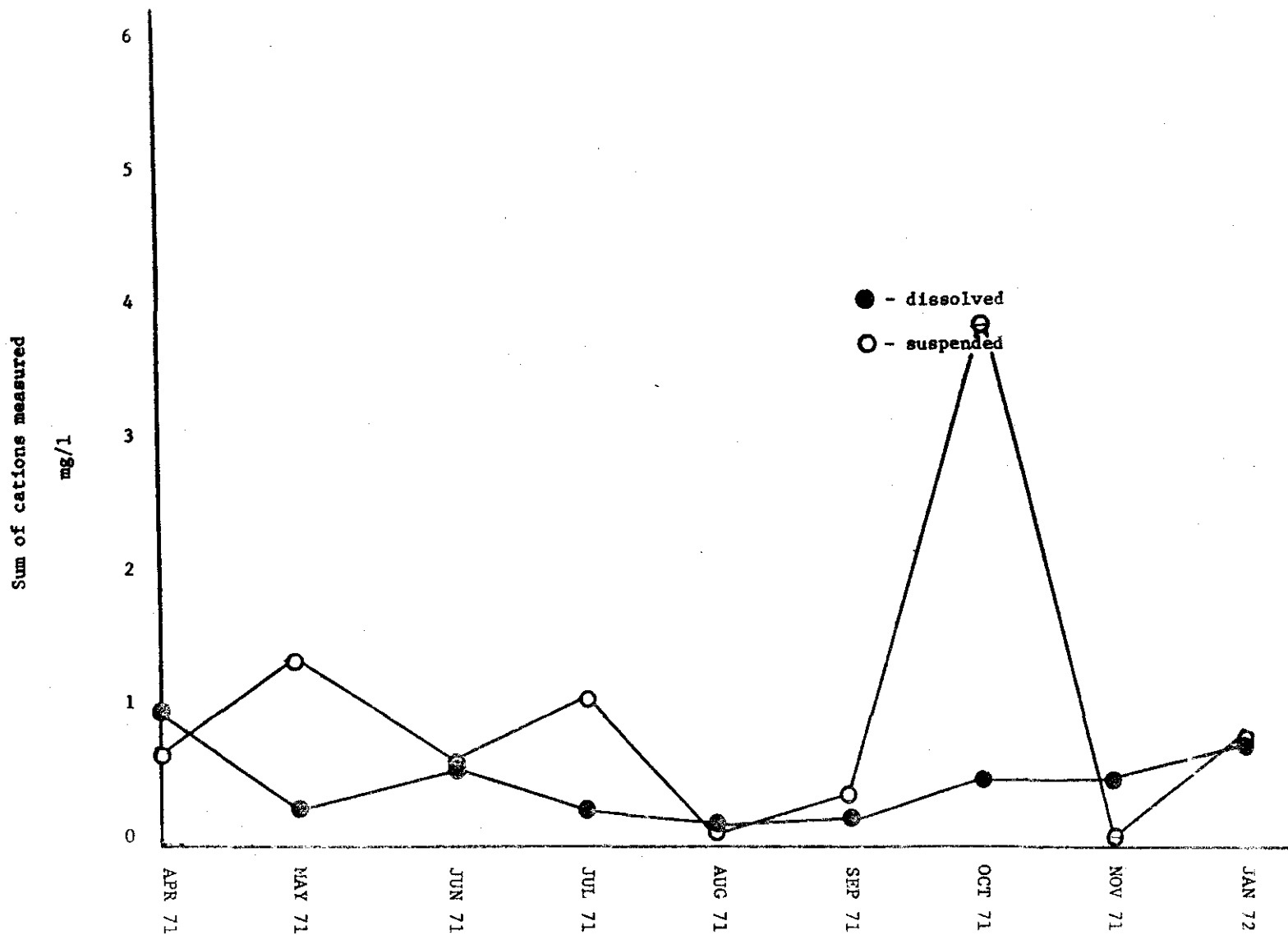
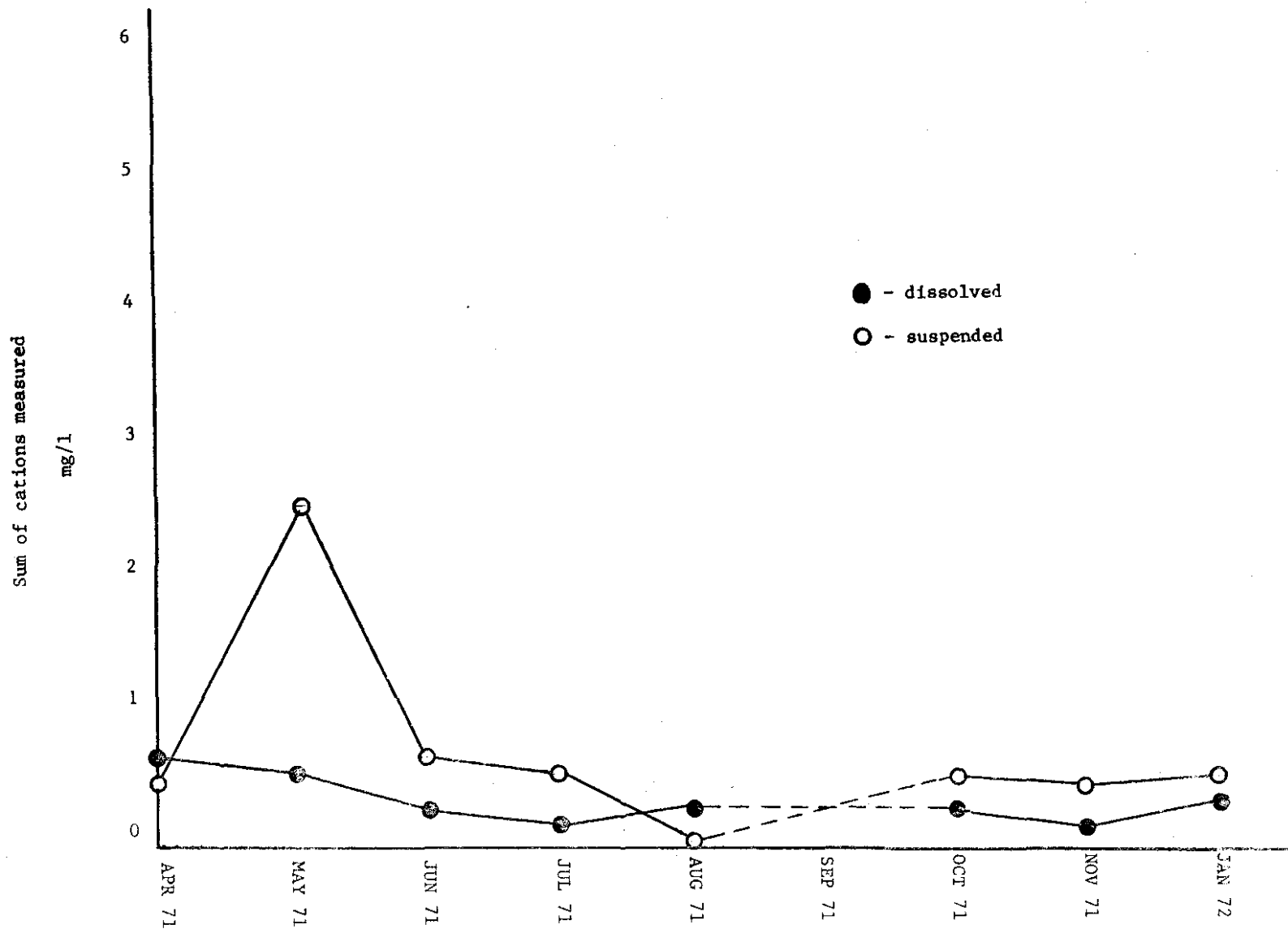


Fig. 40. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.



REFINERY ETU 60.10

Fig. 41. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

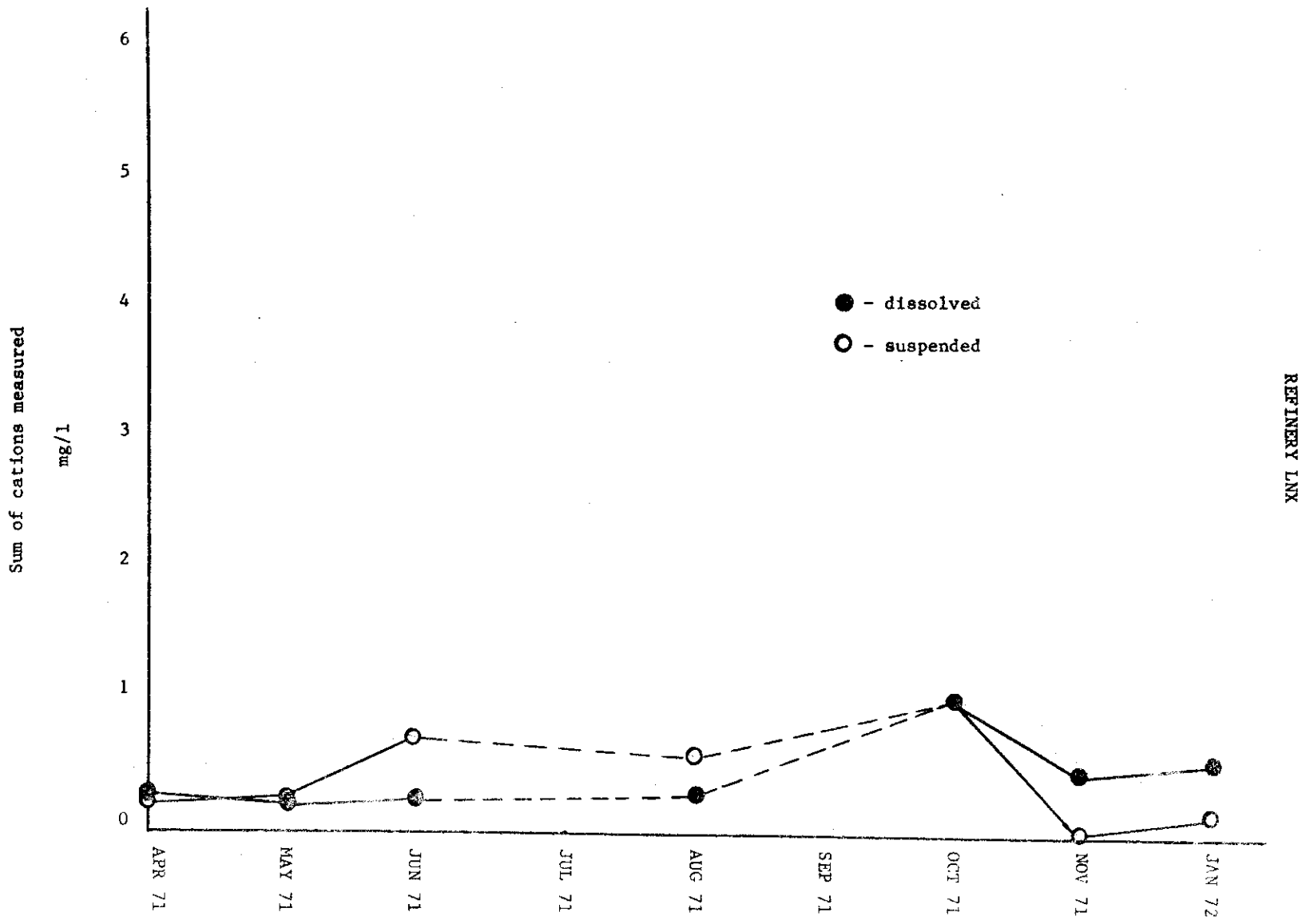


Fig. 42. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

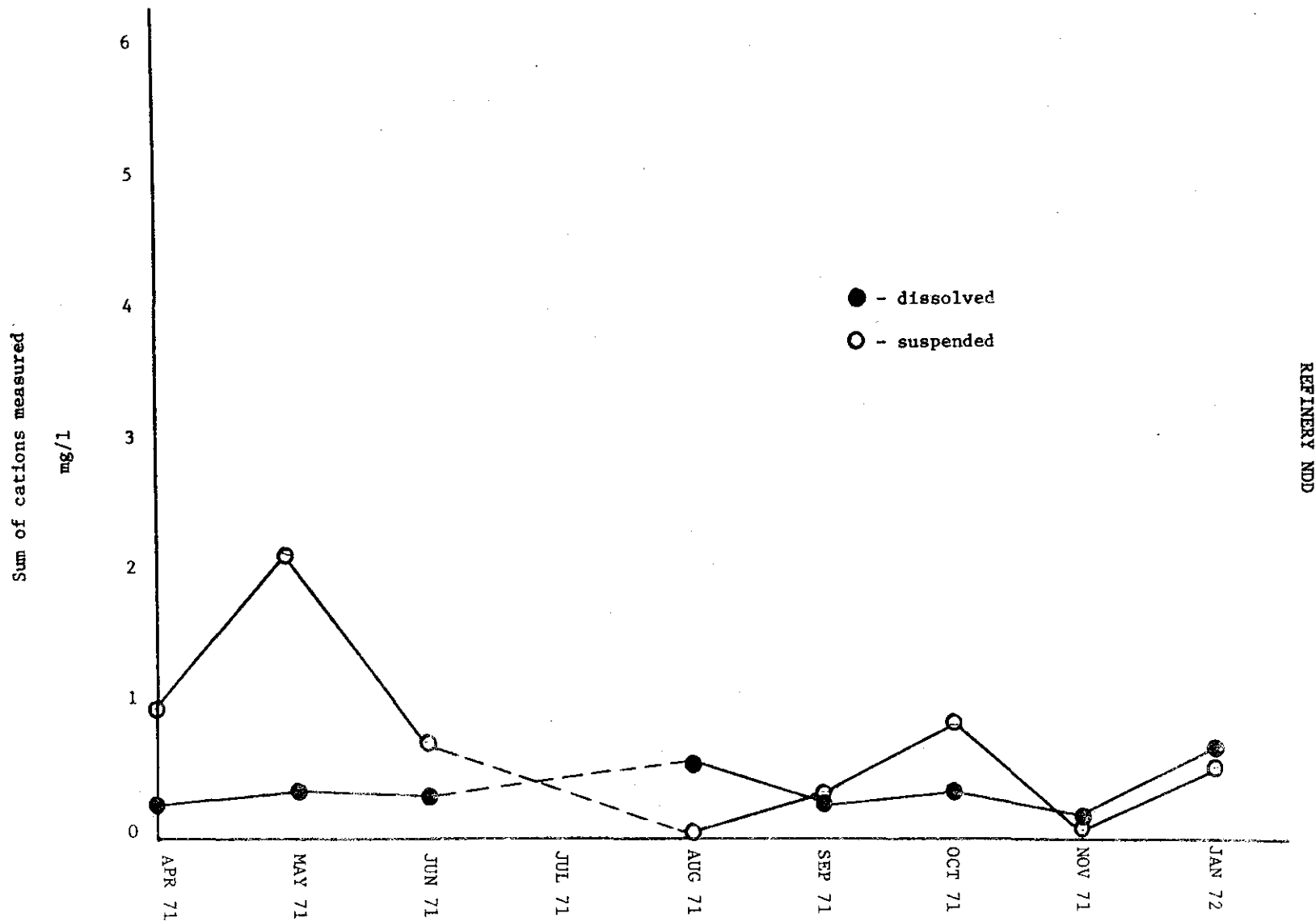


Fig. 43. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

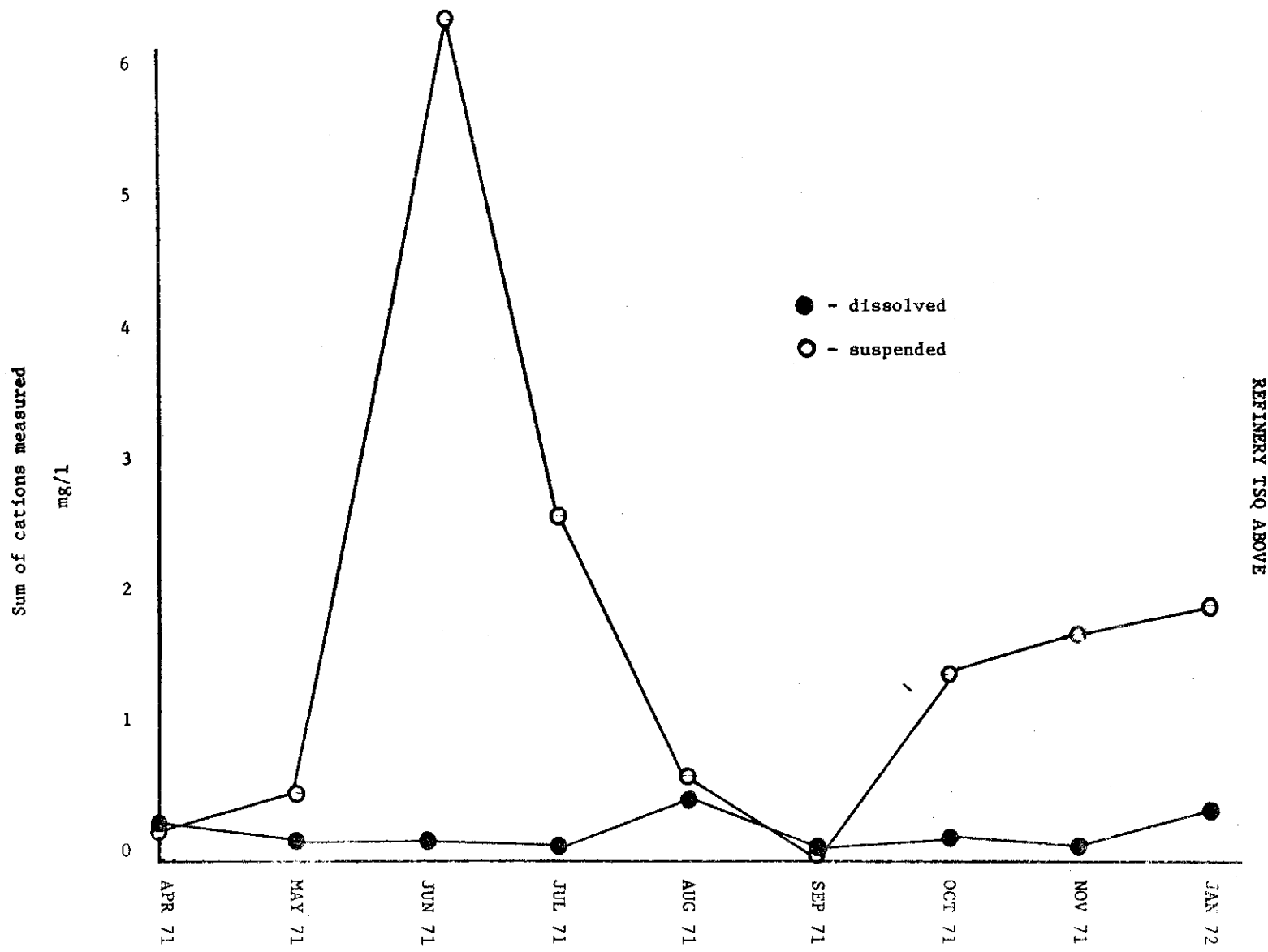


Fig 44. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

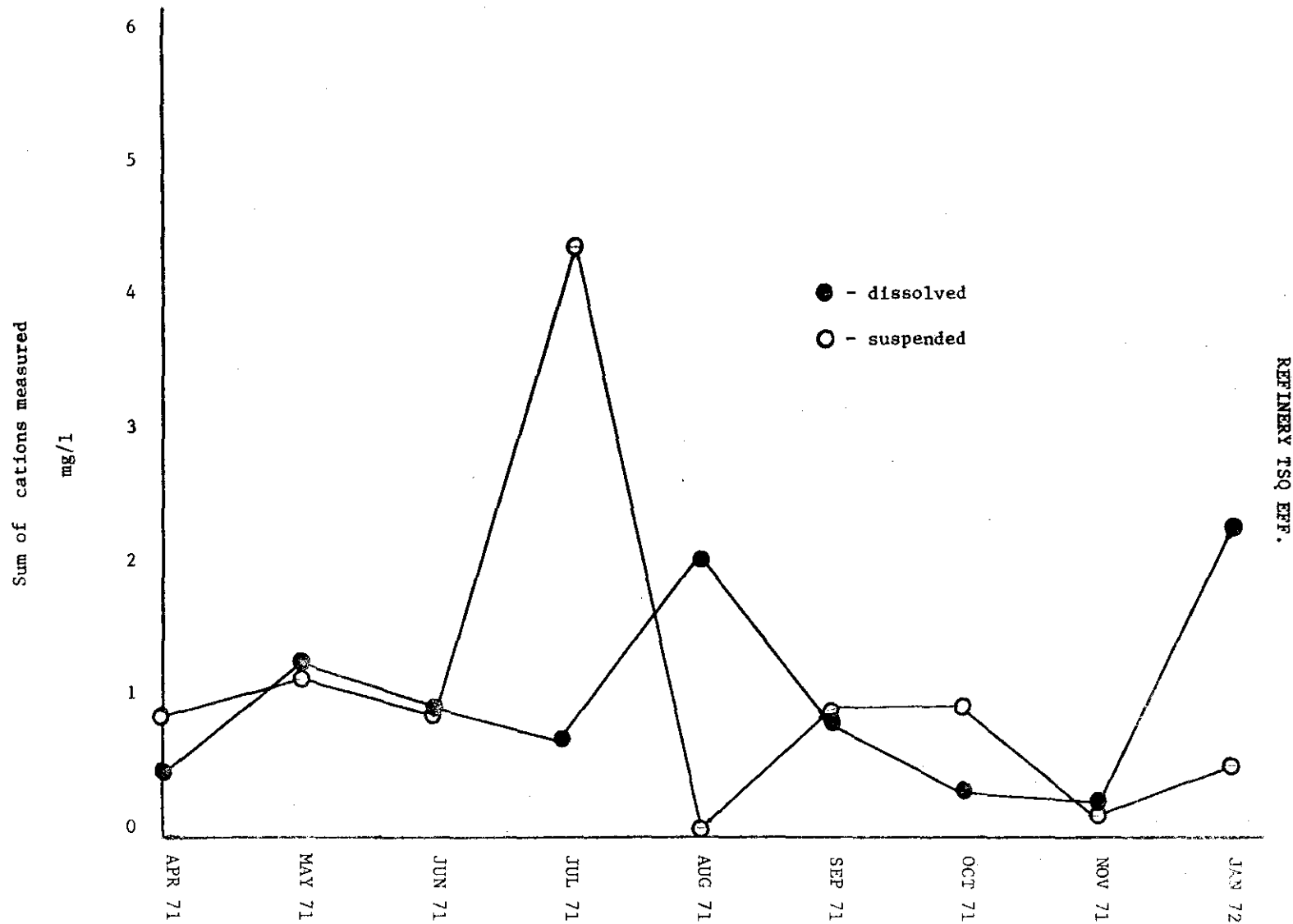


Fig 45. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

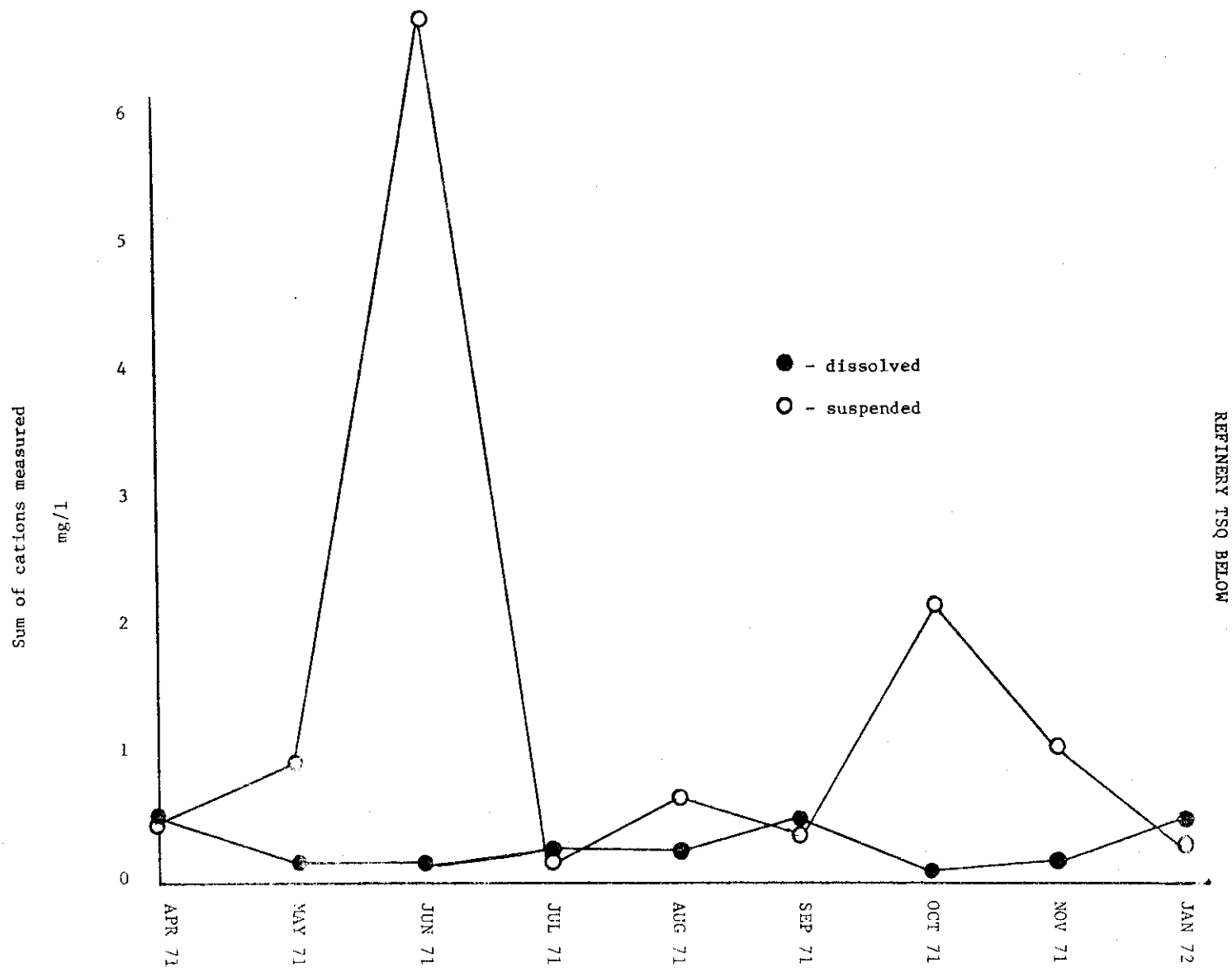


Fig 46. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry.

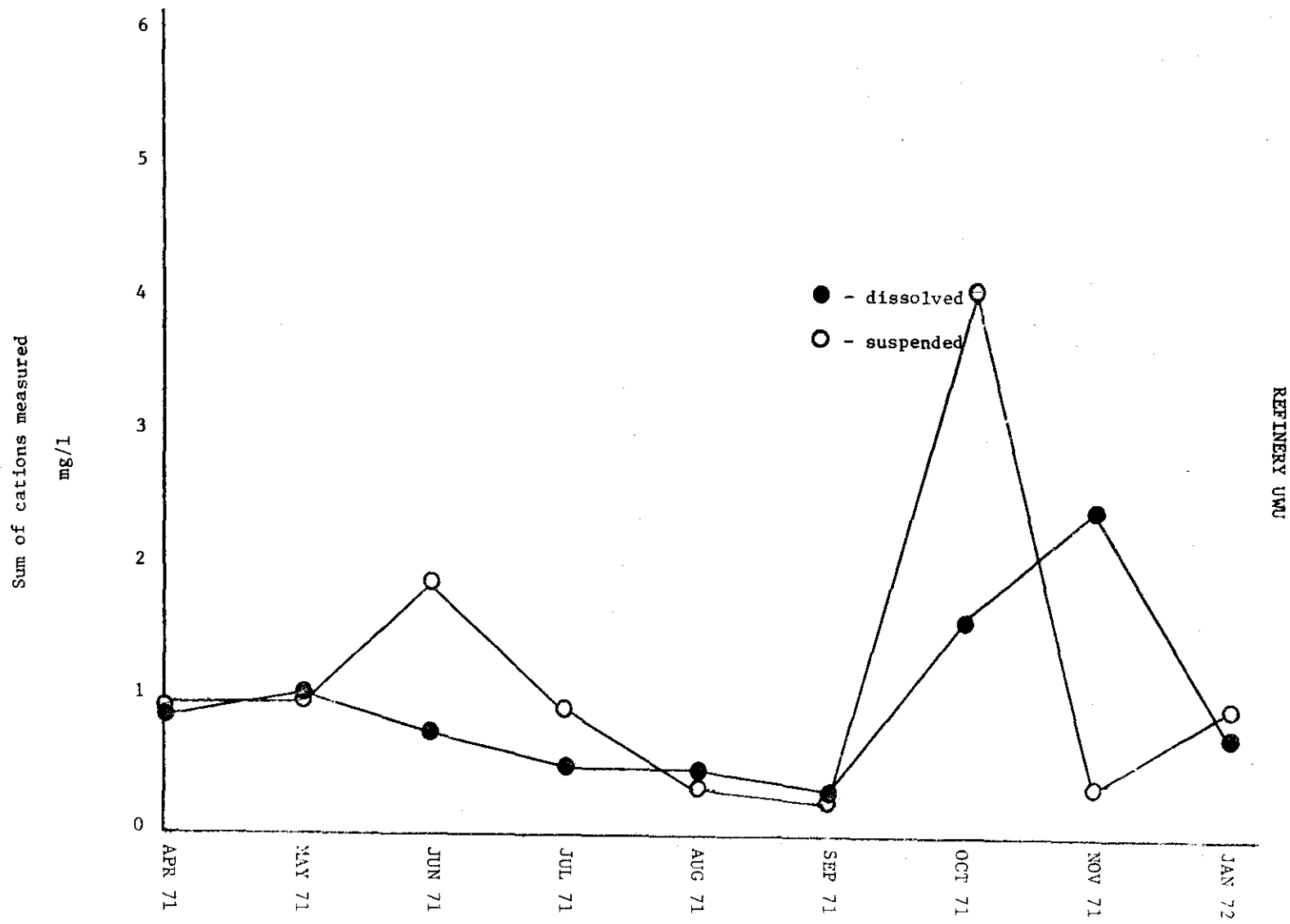


Fig. 47. Seasonal changes in sum of toxic cations in refinery effluents as analyzed by atomic absorption spectrophotometry

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