

DELAYED ANALYSIS OF NITRATE AND PHOSPHATE
IN SEA WATER

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A
THESIS

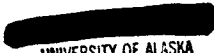
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ABSTRACT

Investigators assume that Hg^{+2} will inhibit biological activity in samples which cannot be immediately analyzed for $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$. To test the validity of this assumption various concentrations of Hg^{+2} , combined with freezing and refrigeration were tested on aliquots of six large samples (15ℓ) of sea water, each of which was obtained with a single large sampler. Immediate analysis for $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ produced initial values which could be statistically compared with the *ca* 120 treated aliquots analyzed at 24 and 36 hour, and six month intervals. Significant variances in concentration could then be identified and associated with the form of preservation used.

The results indicate that the forms of preservation used were neither effective nor reliable. Though Hg^{+2} , refrigeration and freezing are not adequate for the preservation of specific fractions of P and N in sea water, they are effective enough to be used in relationship to gross seasonal water column changes.

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INTRODUCTION

The *in situ* concentrations of phosphate and nitrate need to be known very accurately to better understand their roles in sea water. This study attempts to assess the ability of the most commonly used preservation techniques to give the accurate data which is needed.

Role of $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ in Sea Water

Many marine ecologists have studied the assimilative and regenerative processes of nitrogen and phosphorus forms in the oceans; their findings have been discussed by Sverdrup *et al.* (1942), Raymont (1963), Redfield *et al.* (1963), Vaccaro (1965), Harvey (1966), Chamberlain and Shapiro (1969), Broecker (1974) to name just a few. Broecker (1974) has calculated the balance of biolimiting elements in the sea and postulates that 95 percent of all the phosphorus and nitrogenous compounds reaching the surface waters are consumed within the top warm euphotic layer which comprises one-twentieth of the total oceanic volume. While surface sea waters are seasonally depleted of these nutrients, upwelling of nutrient rich deep waters, particulates falling into the deep ocean, and river and continental run off renew the nonconservative nitrogen and phosphorus to surface waters. The most important consumers of the biolimiting inorganic substances in the marine environment are plants, the primary producers (Sverdrup *et al.*, 1942). These grow only in the euphotic zone, therefore the fact that nutrients can be limiting to primary producers constitutes a real limitation to the animals subsisting on

this production (Sverdrup *et al.*, 1942). In fact, Broecker (1974) points out that "... in their quest for the limiting building blocks, plants appear to 'process' the entire volume of surface ocean water several times each year"; Duursma (1961) suggests up to seven or eight cycles a year.

Deep ocean waters have a P:N:C ratio of 1:16:800 (Broecker, 1974) while that of plants, animals and surface waters is 1:16:106 (Redfield *et al.*, 1963). As proposed by Broecker (1974) and confirmed by the GEOSECS data of Brewer *et al.* (1975) the phosphorus and nitrogen cycle control the amount of organic carbon entering the sediments.

Nitrogen and phosphorus vary greatly in space and time, with oceanic productivity very dependent upon these variations. They do control other cyclic ocean processes, i.e., carbon cycling. Therefore, we should certainly attempt as much perfection as possible in the analysis for these components. The sophisticated equipment now available should encourage great concern for each step from ocean to laboratory. Sampling techniques, analytical procedures as well as initial treatment of all water samples should be carefully scrutinized, to assure that the ocean to laboratory step is as carefully done as are the analytical techniques employed once the samples are in the laboratory.

Background

About 12 years ago the advent of automated techniques made ship-board analysis practical and the validity of preservation techniques for sea water could be tested. Immediate analysis is the best procedure according to the literature. Since this is not always practical,

practical, a number of preservation techniques are still being used by many investigators (Table 1).

Nutrient concentrations appear to change with storage and time making investigators suspicious of delayed nutrient analysis. Zobell and Brown (1944), Murphy and Riley (1956), Barnes (1959), Rainwater and Thatcher (1960), and Harvey (1966) point to microbacterial activity as the cause of changes in phosphorus and nitrogen forms with storage. Lee (1967) believes that the storage bottle is the chief cause of change. Harvey (1966), Murphy and Riley (1956), and Barnes (1959) also implicate enzymatic activity. Harvey (1966) questions that the small numbers of bacteria in filtered sea water could cause such comparatively large changes in stored samples.

Zobell and Brown (1944) used oxygen consumption, bacterial multiplication, nitrate reduction and ammonia production as criteria for bacterial activity in stored sea water. After testing toluol, phenol, tricresol, formaldehyde, chloroform, carbon disulfide, ether, hydrochloric and sulfuric acid, they found nearly all water samples could be preserved by 0.5 percent phenol, a combination of 0.6 percent phenol and 0.5 percent chloroform and acid which would not interfere in subsequent analysis.

Murphy and Riley (1956) after trying a number of preservation methods settled on glass bottles with chloroform for phosphate. Barnes (1959) states that nitrate should be analyzed within 24 hours, if not then glass bottles with mercuric chloride or chloroform should be used for filtered samples. Cool storage, and protection from light and physical disturbance are considered important by Rainwater and Thatcher

(1960). Jenkins (1968) tried a number of preservation techniques for unfiltered estuarine water; refrigeration, freezing, acid and mercuric chloride for nitrogen compounds; glass bottles under refrigeration and freezing plus mercuric chloride and chloroform for phosphate forms.

His results are reproduced in Figure 1.

Heron (1962) demonstrated that lake water reactive phosphate could be preserved in polyethylene bottles pretreated with a solution of iodine in potassium iodide. He also found that immediate filtration and freezing in a dry ice - alcohol mixture was quite effective.

The Federal Water Pollution Control Administration (FWPCA), Chemical Analysis for Water Quality, Training Manual (1968) proposes chloroform, sulfuric acid, quick freezing, mercuric chloride, formalin, potassium cyanide and thymol in various concentrations for specific analysis. Strickland (1958) suggests only quick freezing at -20°C . With the exception of ammonia, Strickland and Parsons (1968) consider quick freezing to be the best compromise. Standard Methods for the Examination of Water and Wastewater, Editions 11 (1960) and 12 (1965) state that sulfuric acid and chloroform are sufficient. FWPCA, Methods for Chemical Analysis of Water and Wastes (1969), and FWPCA, Analytical Techniques for the National Eutrophication Research Program (1969) use mercuric chloride, chloroform and sulfuric acid with the reservation that further research is needed to determine the best preservation for each analysis. Only refrigeration for nitrite is suggested by the annual Book of American Society for Testing and Materials (ASTM) Standards (1970); nothing is proposed for the remaining nutrient analyses. The International Biological Program (IBP) Methods for Chemical Analysis

of Fresh Water (1970), recommends chloroform for nitrate, freezing for reactive phosphate and acid for ammonia.

Olsen (1967) briefly mentions toluene, chloroform and sulfuric acid as preservatives for phosphorus standards while Lee (1967) suggests freezing and mercuric chloride as satisfactory. Lee (1967) believes that chloroform for phosphorus and sulfuric acid for nitrogen do not preserve the original forms of the elements in samples and in fact, might alter them more than simple refrigeration.

PROCEDURES

Sample storage bottles received special attention although they had been in use for several years. After soaking with 10 percent HCl, three portions deionized distilled water, aged sea water (20 percent salinity) and again with deionized distilled water they were thoroughly dried.

To avoid the use of artificial sea water, surface sea water was collected, aged and filtered. This contained no measurable $\text{NO}_3\text{-N}$ or $\text{PO}_4\text{-P}$ and was used for standards and baselines. Standards with and without Hg^{+2} were prepared each day of operation.

Fifteen liters of water were obtained from three depths at two stations, Prince William Sound (PWS) $60^\circ 34.8'\text{N}$, $146^\circ 55.0'\text{W}$ and the Gulf of Alaska (GAK) $59^\circ 9.4'\text{N}$, $147^\circ 6.8'\text{W}$. At each station, samples were taken from three different depths: from the euphotic zone (I); within the thermohalocline (II); and near maximum depth (III). The water was filtered (0.45μ membrane) and divided into 22 125-ml bottles. From three HgCl_2 stock solutions, 0.5 ml was repipetted into the

samples to give concentrations of 10, 40 and 80 mg Hg⁺²/l sample.

Four aliquots were analyzed immediately, zero time, one contained no Hg⁺², three had the above concentrations. Half the remaining bottles were frozen at -20°C and the rest refrigerated at 4°C, then analyzed at intervals of 24 and 36 hours and 6 months.

The data were statistically analyzed using the Biomedical General Hypothesis program, BMDX64. The program simultaneously tests the following hypothesis at a significance level of $\alpha = 0.05$.

H_{time} : mean concentration at time zero, 24 hours, 36 hours and 6 months are identical.

$H_{\text{Hg}^{+2}}$: mean concentrations at 10, 40 and 80 mg/l are identical.

$H_{\text{Temperature}}$: mean concentrations for frozen and refrigerated are identical.

A number of interactions Time x Hg⁺², Time x Temperature, Hg⁺² x Temperature and Time x Hg⁺² x Temperature were also tested. Finally if H_{Time} , $H_{\text{Hg}^{+2}}$, or $H_{\text{Temperature}}$ were rejected, i.e., not all mean concentrations were identical, a series of tests was done to determine which pairs differed significantly.

Reactive phosphate and nitrate concentrations were measured by Strickland and Parsons (1968) automated nutrient procedures except that for phosphate a forty foot time delay coil was inserted ahead of the colorimeter and for nitrate a Cd-Hg amalgamated reducing column was used.

RESULTS

The data from each analysis, zone, depth and station are presented in Tables 2-13 and graphically in Figures 2-13. Least squared analysis of all standards are shown in Table 14. The results of the analysis of variance is shown in Appendix I.

DISCUSSION

Removing a portion of sea water from its natural place in a dynamic system, filtering, preserving and confining it within discrete limits seems to significantly perturb the balance of the waters chemical and biological systems. The water samples from each zone were treated in a consistent manner. What then, caused the inconsistent preservation results from zone to zone and station to station? It would appear that the forms of preservation used were neither effective nor reliable.

Regardless of temperature the first 24 hours appear to be the most critical storage period for $\text{PO}_4\text{-P}$ and to a lesser extent for $\text{NO}_3\text{-N}$. The changes in concentration are statistically significant in all but a few samples. Surprisingly, significant changes occurred during some zero time analyses, which were completed within 30 minutes of triggering the sampler.

The uncertainty in the analysis of each aliquot (Tables 2-13) is expressed as S, standard error of the mean. Change in concentration is shown in terms of Δ , with the variation (v) in each as $\pm\sqrt{v(\Delta)}$ where:

$$\Delta = M_t - M_o, \quad \pm\sqrt{v(\Delta)} = \pm \frac{(S_t)^2}{n} + \frac{(S_o)^2}{n}$$

and M = mean concentration of each aliquot ($\mu\text{g-at}/\ell$)

t = treated aliquot

o = zero time, no Hg^{+2} aliquot

S = standard error of the mean

n = number of determinations (2 unless otherwise indicated)

v = variation.

As a matter of routine the aliquots for zero time were analyzed in the following order: (1) untreated, no Hg^{+2} , (2) 10, (3) 40, and (4) 80 mg/ℓ Hg^{+2} .

Reactive (Ortho) Phosphate

In spite of quite large standard error of the means which occurred in the $\text{PO}_4\text{-P}$ analyses, most changes in concentration were statistically valid. The changes occurring within three zero time periods were unexpected and suggest that in some cases the rate of change may be faster than previously noted. There is certainly the possibility that Hg^{+2} itself has complicated the problem as to how these changes might be mediated. Time, Hg^{+2} concentration and storage temperature were significant for almost all phosphate storage conditions in both stations and all zones with the exception of PWS, zone II, where storage temperature was not significant (see Appendix I, p. 44).

Zone I, GAK, $\text{PO}_4\text{-P}$ (Table 8) shows a decrease in concentration for zero time (0.65; 0.65; 0.43; 0.37 $\mu\text{g-at}/\ell$ for untreated, 10, 40, and 80 mg/ℓ Hg^{+2} respectively). Yet in the 24 hour analysis $\text{PO}_4\text{-P}$ has increased by *ca* 60 percent. By contrast zone III, GAK, $\text{PO}_4\text{-P}$

(Table 12) increased within the zero time period. In this zone the mean, untreated, zero time $\text{PO}_4\text{-P}$ concentration was $2.62 \mu\text{g-at}/\ell$ and consisted of three determinations 2.45 , 2.56 and $2.86 \mu\text{g-at}/\ell$, analyzed sequentially. The mean concentration for zero time, $80 \text{ mg}/\ell$ Hg^{+2} was $3.48 \pm 0.10 \mu\text{g-at}/\ell$. Again the 24 hour $\text{PO}_4\text{-P}$ increased, *ca* 50 percent. Prince William Sound, zone II (Table 4) had an increase in $\text{PO}_4\text{-P}$ concentration of *ca* 120 percent in the first 30 minutes.

Concentrations of dissolved organic phosphorus may decrease with depth, especially below depths of 1000 m, and the concentration in surface water can exceed that of reactive (ortho)-phosphate (Ketchum *et al.*, 1955). Not all organic and polyphosphorus compounds are likely to hydrolyze at the same rate since some are more labile than others. In addition, the ratio of the various forms of phosphorus and nitrogen can differ with depth and location (Duursma, 1961).

Some of the organics in the samples could be of bacterial origin which would represent the "surplus" phosphate of Barsdate *et al.* (1974) and account for the increase, in some cases, for $\text{PO}_4\text{-P}$ in the zero to 24 hour periods. Prentki and Barsdate (1975) have shown that Hg^{+2} at 4 ppm inhibits phosphatase activity in lake waters. They suggest temperature and possibly the concentration of reactive colloids are related to the rate of change in reactive phosphorus. These factors may explain the increase in 24 hour concentrations for zone I, GAK, $\text{PO}_4\text{-P}$ (Figure 9) and zone II, PWS, $\text{PO}_4\text{-P}$ (Figure 5). However, the fairly consistent decrease in $\text{PO}_4\text{-P}$ for the 36 hour period is puzzling. It would be expected that the same process or processes which cause the increase in the 24 hour period would be in operation at 36 hours,

but this might be the period of utilization of $\text{PO}_4\text{-P}$ by bacteria as suggested by Harvey (1966).

Reactive Nitrate

In contrast to $\text{PO}_4\text{-P}$, the $\text{NO}_3\text{-N}$ concentration changes were generally negative and most were also statistically valid. Enzymatic nitrate reduction, adsorption on bottle walls or by colloids and the Hg^{+2} itself could possibly cause the losses. Hg^{+2} at the three concentrations used was significant only in PWS, zone II and GAK, zone I (see Appendix I, p. 44 and 46). PWS, zones II and III (Tables 5 and 7) suggest that there is an increased loss of $\text{NO}_3\text{-N}$ with time at both storage temperatures, however storage temperature was significant for only GAK, zone III (see Appendix I, p. 48). For these two zones, PWS II and III (see Appendix I, p. 44 and 45) all time interactions were significant with the exception of the 24 to 36 hour (Time 23) period. The remaining zones in PWS and GAK show a lesser degree of nitrate loss with time, however time was significant for most of these changes.

In this study, it was assumed that zero time, no Hg^{+2} , analyses represented the most accurate value for *in situ* concentrations of $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$. These zero time, no Hg^{+2} , analyses represent a lag time of *ca* 10 minutes zones I and II to *ca* 20 minutes, zones III, after closing the sampler. While Chamberlain and Shapiro (1969), in their study of the biological significance of phosphate analyses, did filter their samples as soon as possible, 6 hours elapsed before their initial analyses were completed. This may be why their work neither confirmed nor denied the possibility that labile phosphorus, which

could be hydrolyzed during analysis, might be present in filtrates of lake waters. Jenkins (1968) also introduced a lag time into his preservation experiment on unfiltered estuarine waters. The mixing of large volumes from several samplings to obtain representative aliquots could take several hours. He obtained fairly good results with 40 mg/l Hg^{+2} at 4°C storage for $\text{PO}_4\text{-P}$ and 2 mg/l of 5 percent sulfuric acid for $\text{NO}_3\text{-N}$ preservation. Glass bottles with 40 mg/l Hg^{+2} at -10°C storage for $\text{PO}_4\text{-P}$ produced excellent results which we were unable to duplicate. Storage on shipboard was hardly quiescent which Jenkin (1968) and Rainwater and Thatcher (1960) consider very important. The plots of Jenkins (1968) (Figure 1), resemble ours (Figures 4-13). His lapsed times are very different, yet the concentration changes are similar. This might suggest that storage time itself may not be as big a factor as processes taking place when samples thaw or warm to room temperature preceeding analysis.

CONCLUSIONS

The statistical analysis of these data (Appendix I) suggests that Hg^{+2} concentrations and storage temperature are significant to the preservation of original $\text{PO}_4\text{-P}$ concentrations; the one exception is zone II PWS-2 where storage temperature was insignificant. With the exception of zone III, GAK, storage temperature was an insignificant factor in the preservation of $\text{NO}_3\text{-N}$ concentrations and Hg^{+2} was significant for only zone II, PWS-2 and zone I, GAK nitrates. Time was significant for $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ in both stations and all zones.

Delayed nutrient analysis is adequate for determining the concentration structure of seasonal $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ within a body of seawater. However, other methods of preservation need to be investigated in order to reliably assess the various fractions, organic and inorganic, within the total phosphorus and nitrogen regime.

TABLE 1
Preservation Methods.

	-20°C	-10°C	4°C	HgCl ₂	HgCl ₂ 4°C	HgCl ₂ -10°C
American Public Health Assoc. 1960, 1965	NO ₃ -N	-	-	-	-	-
Annual Book of ASTM Standards, 1970	-	-	SiO ₄ -Si	-	-	-
Barnes, 1959	-	-	-	NO ₃ -N glass bottles	-	-
FWPCA, Eutrophication Program, 1969	NO ₃ -N PO ₄ -P	-	-	PO ₄ -P	NO ₃ -N NH ₄ -N	-
FWPCA, Method for Chemical Analysis of Water & Wastes, 1969	-	-	-	-	PO ₄ -P NH ₄ -N NO ₃ -N	-
FWPCA, Training Manual, 1968	PO ₄ -P NH ₄ -N NO ₃ -N	-	-	PO ₄ -P	-	-
Heron, 1962	-	-	-	-	-	-
IBP, 1970	PO ₄ -P	-	-	-	-	-
Jenkins, 1968	-	NO ₂ -N NH ₄ -N PO ₄ -P	NO ₃ -N NH ₄ -N PO ₄ -P	-	NO ₃ -N NH ₄ -N PO ₄ -P	PO ₄ -P
Lee, 1967	-	-	-	-	-	-
Murphy & Riley, 1956	-	-	-	-	-	-
Olsen, 1967	-	-	-	-	-	-
Rainwater & Thatcher, 1960	-	-	PO ₄ -P NO ₃ -N Dark, Quiescent	-	-	-
Strickland, 1958	PO ₄ -P NO ₃ -N	-	-	-	-	-
Strickland & Parsons, 1968	PO ₄ -P NO ₃ -N NH ₄ -N*	-	-	-	-	-
Zobell & Brown, 1944	-	-	-	-	-	-

*Reservations concerning attempts to delay NH₄-N analysis.

TABLE 1 (Continued)

	HgCl ₂ -20°C	Sterile Bottles 4°C	H ₂ SO ₄	H ₂ SO ₄ 4°C	Chloro- form
American Public Health Assoc. 1960, 1965	-	-	NH ₄ -N NO ₃ -N	-	PO ₄ -P
Annual Book of ASTM Standards, 1970	-	NO ₂ -N	-	-	-
Barnes, 1959	-	-	-	-	NO ₃ -N glass bottles
FWPCA, Eutrophication Program, 1969	-	-	-	-	NO ₃ -N PO ₄ -P
FWPCA, Method for Chemical Analysis of Water & Wastes, 1969	-	-	-	NH ₄ -N	-
FWPCA, Training Manual, 1968	-	-	NH ₄ -N NO ₃ -N	-	PO ₄ -P NH ₄ -N NO ₃ -N
Heron, 1962	-	-	-	-	-
IBP, 1970	-	-	NH ₄ -N NO ₃ -N	-	NO ₃ -N
Jenkins, 1968	-	-	-	NO ₃ -N NH ₄ -N	PO ₄ -P
Lee, 1967	PO ₄ -P	-	-	-	-
Murphy & Riley, 1956	-	-	-	-	PO ₄ -P glass bottles
Olsen, 1967	-	-	PO ₄ -P	-	PO ₄ -P
Rainwater & Thatcher, 1960	-	-	-	-	-
Strickland, 1958	-	-	-	-	PO ₄ -P
Strickland & Parsons, 1968	-	-	-	-	-
Zobell & Brown, 1944	-	-	-	-	-

TABLE 1 (Continued)

	I ₂ in Solu- tion of KI	Dry ice- alcohol	Toluene	0.5% Phenol	0.5% Phenol +0.5% CHCl ₃
American Public Health Assoc. 1960, 1965	-	-	-	-	-
Annual Book of ASTM Standards, 1970	-	-	-	-	-
Barnes, 1959	-	-	-	-	-
FWPCA, Eutrophica- tion Program, 1969	-	-	-	-	-
FWPCA, Method for Chemical Analysis of Water & Wastes, 1969	-	-	-	-	-
FWPCA, Training Manual, 1968	-	-	-	-	-
Heron, 1962	PO ₄ -P	PO ₄ -P	-	-	-
IBP, 1970	-	-	-	-	-
Jenkins, 1968	-	-	-	-	-
Lee, 1967	-	-	-	-	-
Murphy & Riley, 1956	-	-	-	-	-
Olsen, 1967	-	-	PO ₄ -P	-	-
Rainwater & Thatcher, 1960	-	-	-	-	-
Strickland, 1958	-	-	-	-	-
Strickland & Parsons, 1968	-	-	-	-	-
Zobell & Brown, 1944	-	-	-	PO ₄ -P NH ₄ -N NO ₂ -N NO ₃ -N	PO ₄ -P NH ₄ -N NO ₃ -N NO ₃ -N

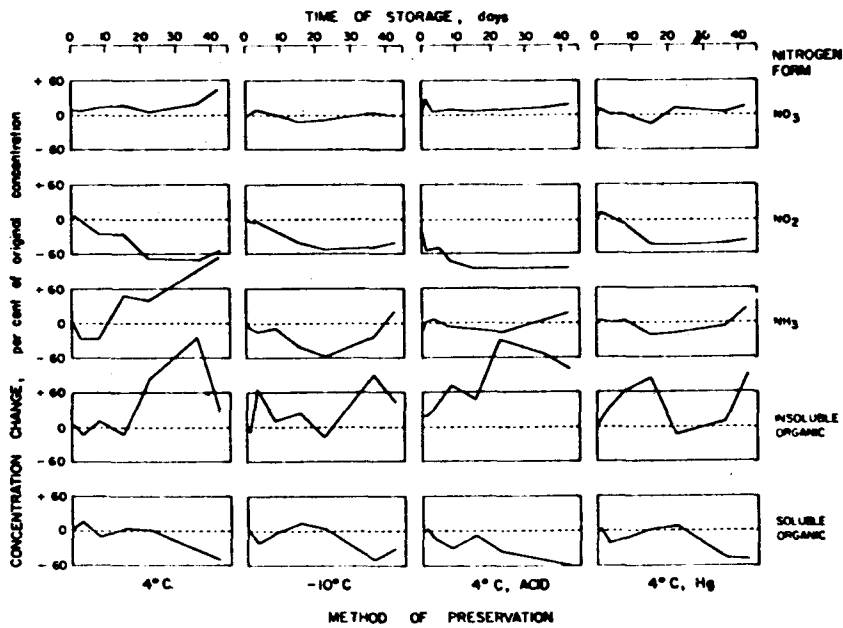
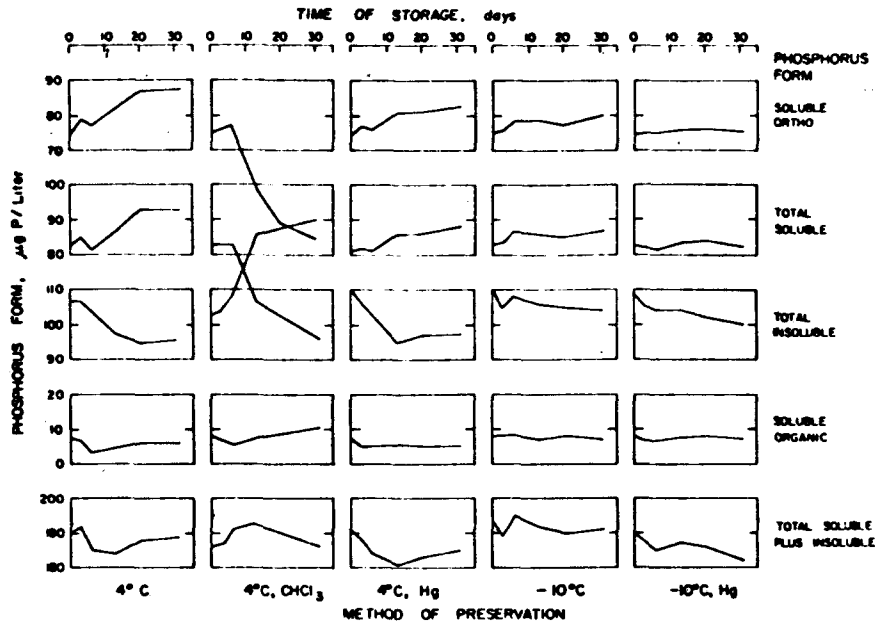


Figure 1. From Jenkins, 1968, p. 278 and 279.

TABLE 2

Prince William Sound, Zone I.

Time of Analysis	PO ₄ -P, Mean Zero Time, No Hg ⁺² = 0.66±0.00 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	0.64±0.00	-0.02±0.00	0.66±0.00	0.00±0.00	0.67±0.01	+0.01±0.01
24 hours	0.73±0.00	+0.07±0.00	0.69±0.00	+0.03±0.00	0.71±0.00	+0.05±0.00
36 hours	0.69±0.00	+0.03±0.00	0.67±0.00	+0.01±0.00	0.67±0.00	+0.01±0.00
6 months	0.64±0.00	-0.02±0.00	0.62±0.03	-0.04±0.02	0.65±0.00	-0.01±0.00
FROZEN						
0 hours	0.64±0.00	-0.02±0.00	0.66±0.00	0.00±0.00 [†]	0.67±0.01	+0.01±0.01
24 hours	0.60±0.00	-0.06±0.00	0.65±0.01	-0.01±0.01 [†]	0.70±0.01	+0.04±0.01
36 hours	0.63±0.00	-0.03±0.00	0.64±0.01	-0.02±0.01	0.61±0.00	-0.05±0.00
6 months	0.60±0.01	-0.06±0.01	0.64±0.01	-0.02±0.01	0.60±0.01	-0.06±0.01

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determination - 3.

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone I

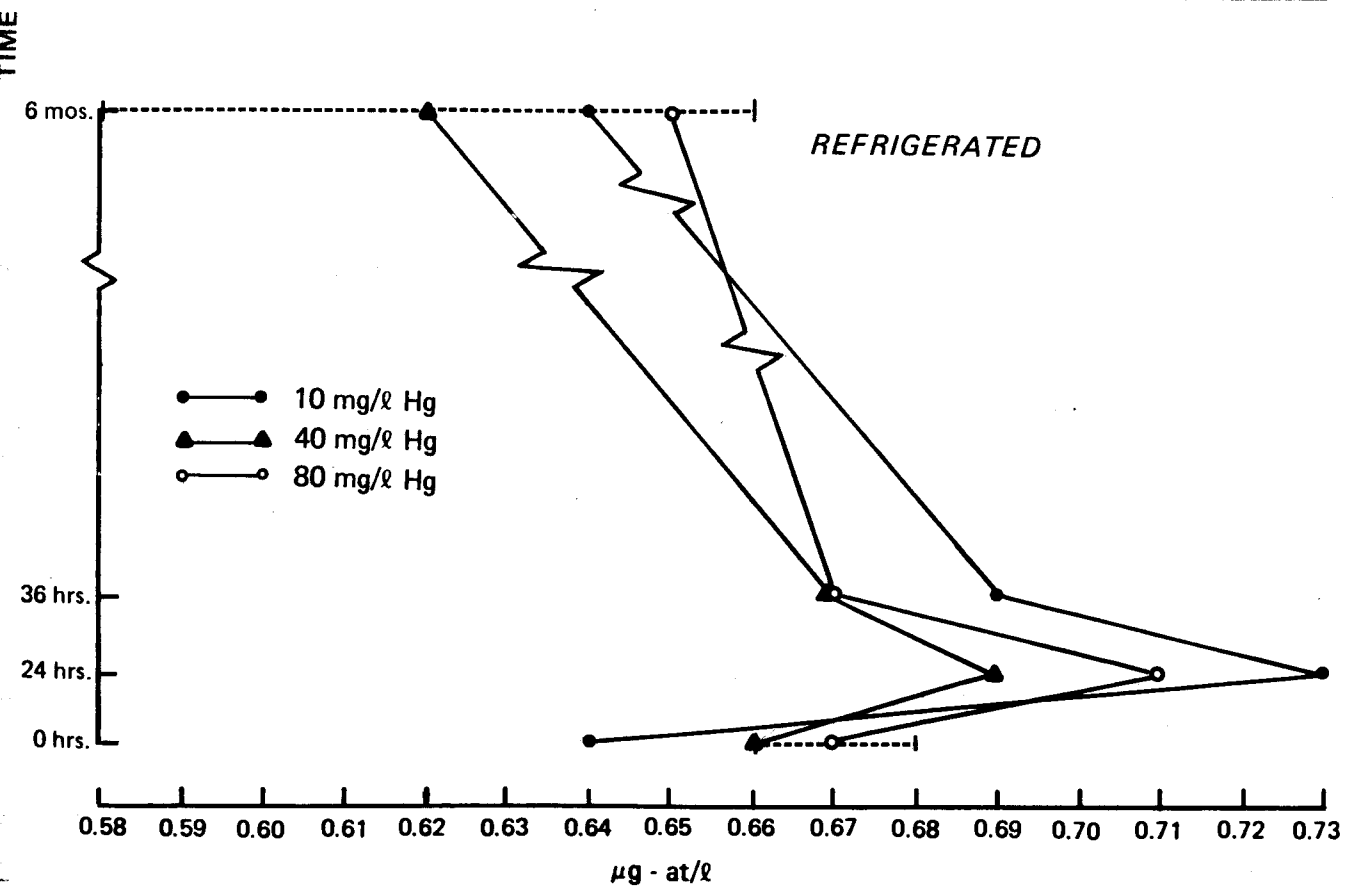
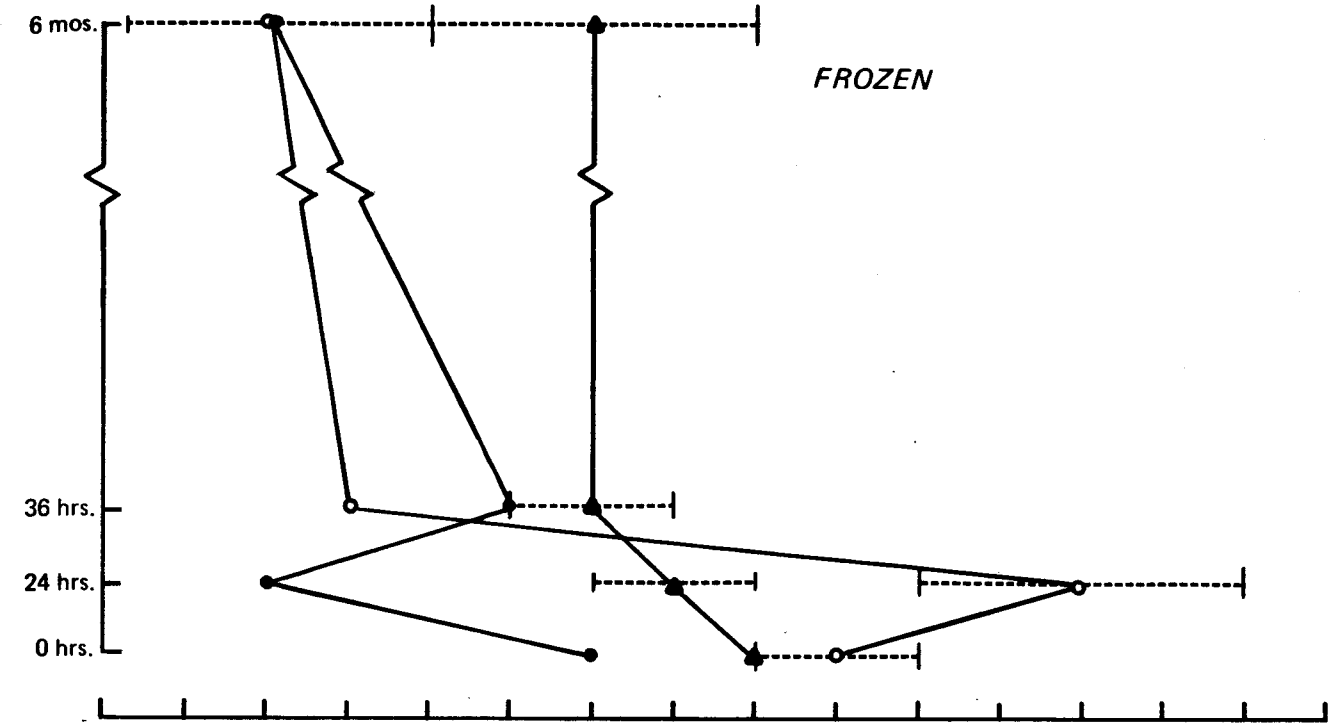


Figure 2. $PO_4\text{-P}$, Mean Zero Time, No, $Hg^{+2} = 0.66 \pm 0.00 \mu\text{g-at/l}$.

TABLE 3

Prince William Sound, Zone I.

Time of Analysis	NO ₃ -N, Mean Zero Time, No Hg ⁺² = 5.52±0.01 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	5.92±0.02	+0.40±0.02	5.71±0.01	+0.19±0.01	5.74±0.01	+0.22±0.01
24 hours	4.84±0.48	-0.68±0.34	5.21±0.02	-0.31±0.02	5.10±0.04	-0.42±0.03
36 hours	5.55±0.05	+0.03±0.04	5.35±0.05	-0.17±0.04	5.30±0.10	-0.22±0.07
6 months	5.30±0.10	-0.22±0.07	5.60±0.10	+0.08±0.07	5.95±0.05	+0.43±0.04
FROZEN						
0 hours	5.92±0.02	+0.40±0.02	5.71±0.01	+0.19±0.01	5.74±0.01	+0.22±0.01
24 hours	5.11±0.11	-0.41±0.08	5.08±0.01	-0.44±0.01	4.39±0.40	-1.13±0.28
36 hours	5.45±0.05	-0.07±0.04	5.35±0.05	-0.17±0.04	5.35±0.15	-0.17±0.11
6 months	5.55±0.05	+0.03±0.04	5.45±0.05	-0.07±0.04	5.45±0.15	-0.07±0.11

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone I

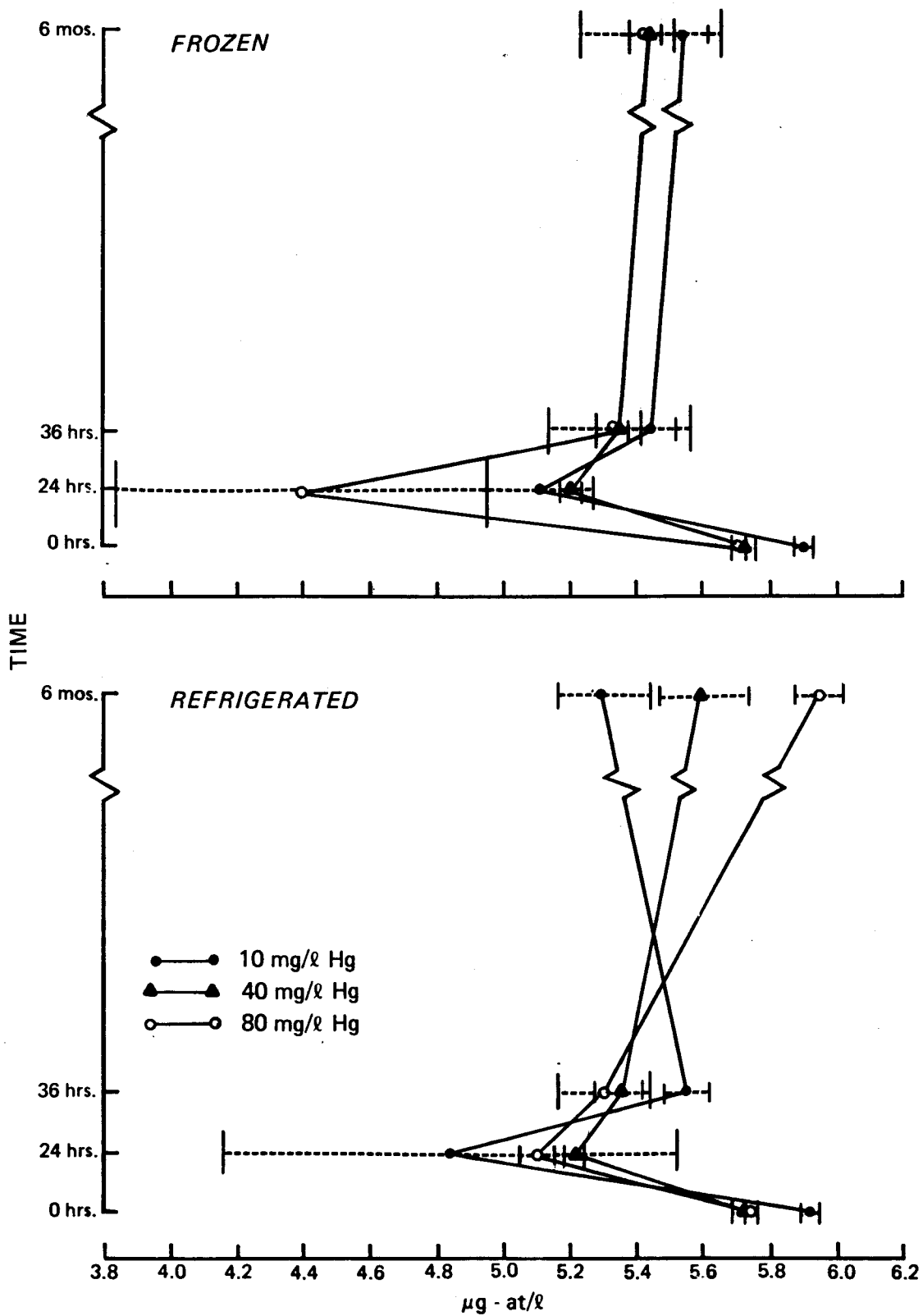


Figure 3. $\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 5.52 \pm 0.01 \mu\text{g} - \text{at}/\ell$.

TABLE 4

Prince William Sound, Zone II.

Time of Analysis	$\text{PO}_4\text{-P}$, Mean Zero Time, No Hg^{+2} = 0.73 ± 0.01 $\mu\text{g-at}/\ell$					
	10 mg/ ℓ Hg^{+2}		40 mg/ ℓ Hg^{+2}		80 mg/ ℓ Hg^{+2}	
	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *
REFRIGERATED						
0 hours	0.86 \pm 0.02	+0.13 \pm 0.02	0.89 \pm 0.01	+0.16 \pm 0.01	1.61 \pm 0.03	+0.88 \pm 0.02
24 hours	1.74 \pm 0.01	+1.01 \pm 0.01	1.67 \pm 0.02	+0.94 \pm 0.02	1.68 \pm 0.01	+0.95 \pm 0.01
36 hours	1.65 \pm 0.00	+0.92 \pm 0.01	1.73 \pm 0.00	+1.00 \pm 0.01	1.65 \pm 0.00	+0.92 \pm 0.01
6 months	- \pm -	- \pm -	1.48 \pm 0.04	+0.75 \pm 0.03	1.30 \pm 0.16	+0.57 \pm 0.11
FROZEN						
0 hours	0.86 \pm 0.02	+0.13 \pm 0.02	0.89 \pm 0.01	+0.16 \pm 0.01	1.61 \pm 0.03	+0.88 \pm 0.02
24 hours	1.71 \pm 0.02	+0.98 \pm 0.02	1.70 \pm 0.01	+0.97 \pm 0.01	1.73 \pm 0.02	+1.00 \pm 0.02
36 hours	- \pm -	- \pm -	1.64 \pm 0.01	+0.91 \pm 0.01	1.69 \pm 0.00	+0.96 \pm 0.01
6 months	1.29 \pm 0.01	+0.56 \pm 0.01	1.36 \pm 0.01	+0.63 \pm 0.01	1.38 \pm 0.10	+0.65 \pm 0.07

* Δ change in relationship to mean zero time concentration which contained no Hg^{+2} .

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone II

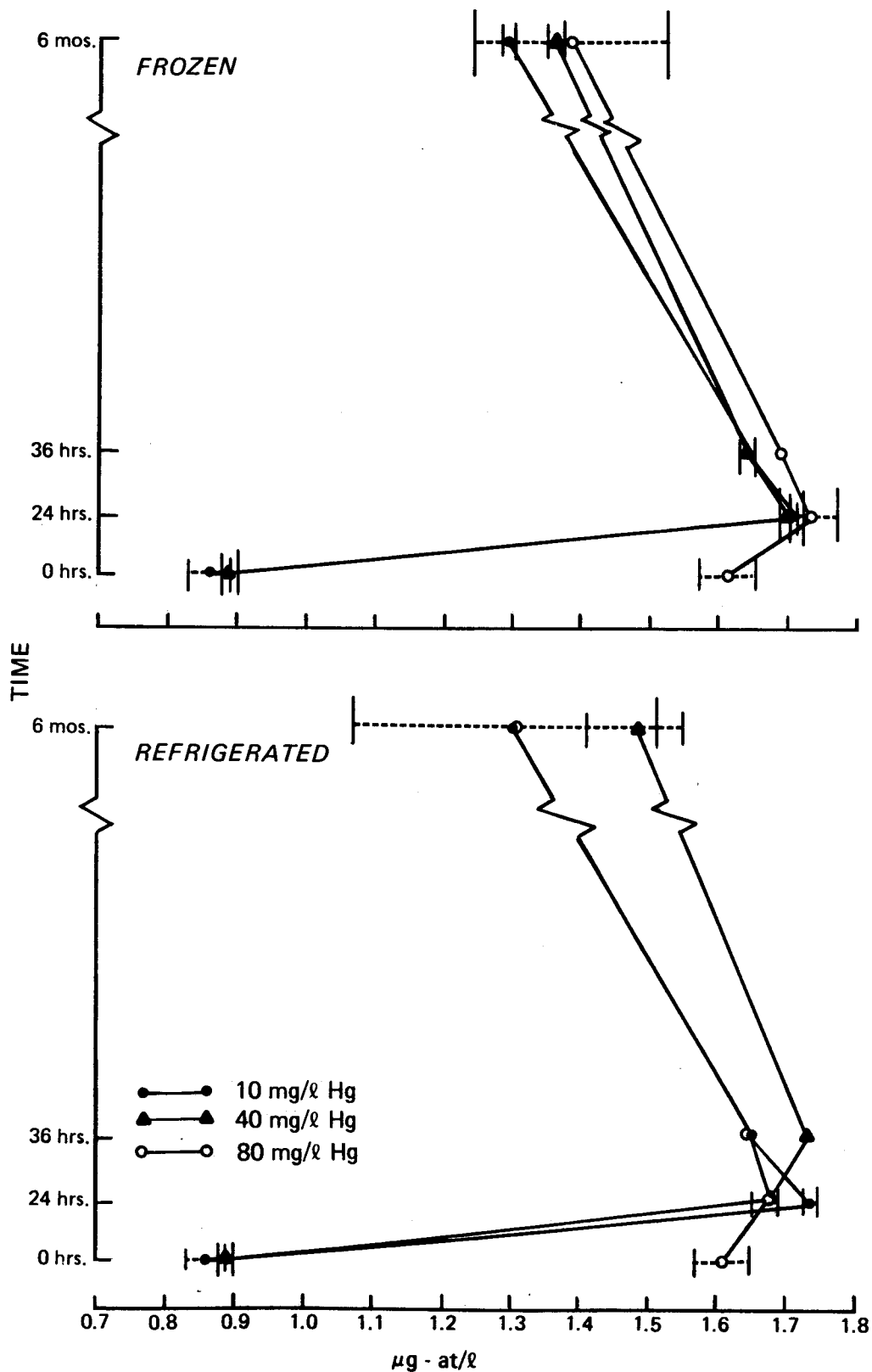


Figure 4. $\text{PO}_4\text{-P}$, Mean Zero Time, No $\text{Hg}^{+2} = 0.73 \pm 0.01 \mu\text{g} - \text{at}/\ell$.

TABLE 5

Prince William Sound, Zone II.

Time of Analysis	$\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 20.6 \pm 0.14 \text{ } \mu\text{g-at}/\ell$					
	10 mg/l Hg^{+2}		40 mg/l Hg^{+2}		80 mg/l Hg^{+2}	
	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *
REFRIGERATED						
0 hours	18.50±0.50	-2.10±0.37	20.00±0.20	-0.60±0.17	18.10±0.60	-2.50±0.44
24 hours	16.75±0.05	-3.85±0.10	17.70±0.10	-2.90±0.12	17.60±0.20	-3.00±0.17
36 hours	17.50±0.10	-3.10±0.12	18.00±1.09	-2.60±0.12	16.95±0.85	-3.65±0.61
6 months	- ± -	- ± -	16.55±0.05	-4.05±0.10	16.50±0.10	-4.10±0.12
FROZEN						
0 hours	18.50±0.50	-2.10±0.37	20.00±0.20	-0.60±0.17	18.10±0.60	-2.50±0.44
24 hours	16.50±0.50	-4.10±0.37	17.45±0.35	-3.15±0.27	17.80±0.10	-2.80±0.12
36 hours	- ± -	- ± -	17.30±0.14	-3.30±0.12 [†]	17.20±0.20	-3.40±0.22
6 months	14.95±0.04	-5.65±0.10 [†]	16.12±0.45	-4.48±0.24 [†]	16.30±0.94	-4.30±0.67

* Δ change in relationship to mean zero time concentration which contained no Hg^{+2} .

[†] Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone II

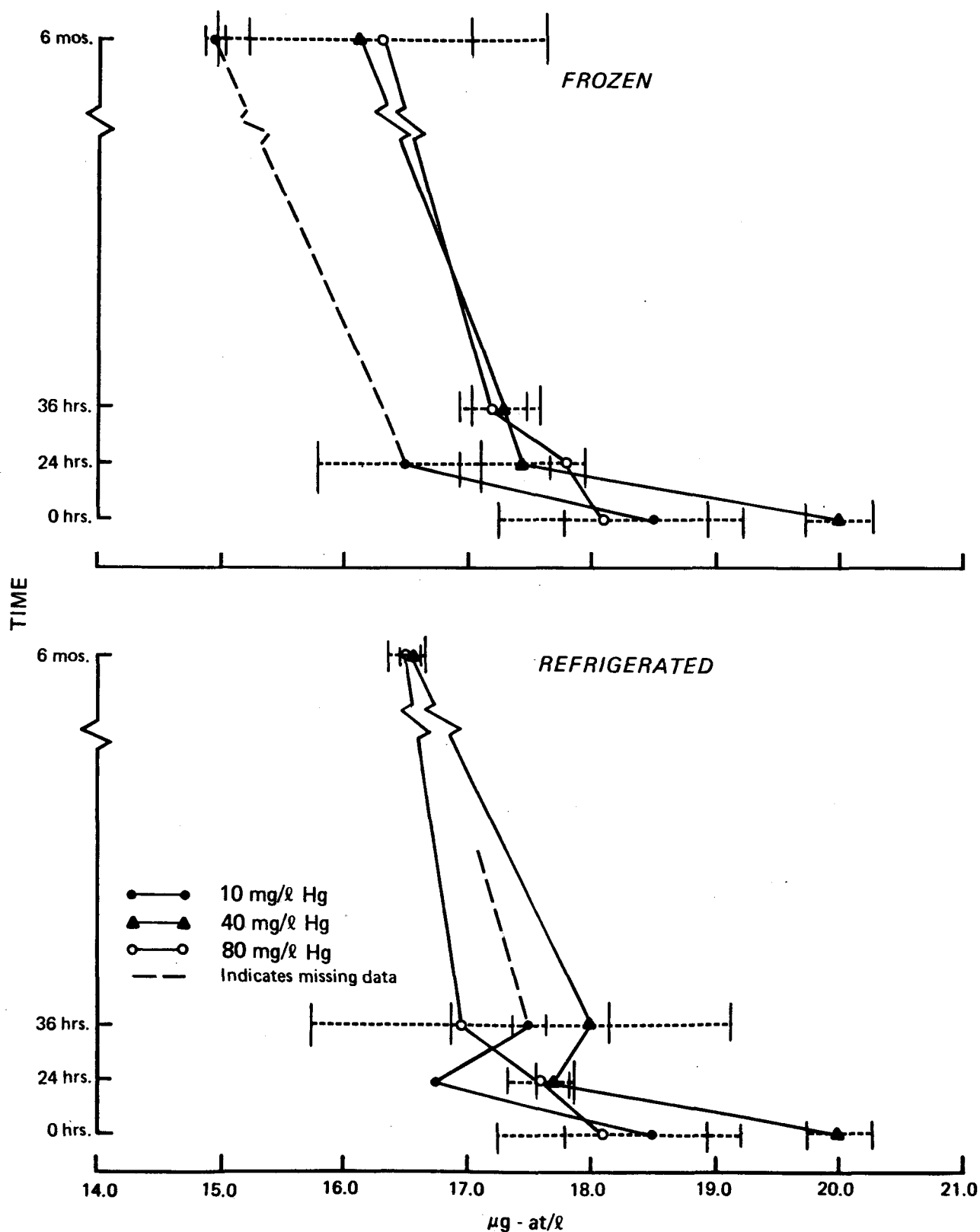


Figure 5. $\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 20.6 \pm 0.14 \mu\text{g-at}/\ell$.

TABLE 6

Prince William Sound, Zone III.

PO ₄ -P, Mean Zero Time, No Hg ⁺² = 2.31±0.02 µg-at/l						
Time of Analysis	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	2.31±0.01	0.00±0.02	2.33±0.01	+0.02±0.02	2.37±0.01	+0.06±0.02
24 hours	2.32±0.01	+0.01±0.02	2.28±0.01	-0.03±0.02	2.34±0.01	+0.03±0.02
36 hours	2.19±0.01	-0.12±0.02	2.30±0.01	-0.01±0.02	2.17±0.00	-0.14±0.01
6 months	0.44±0.01	-1.87±0.02	1.98±0.01	-0.33±0.02	2.02±0.01	-0.29±0.02
FROZEN						
0 hours	2.31±0.01	0.00±0.02	2.33±0.01	+0.02±0.02	2.37±0.01	+0.06±0.02
24 hours	2.42±0.00	-0.11±0.01	2.40±0.00	+0.09±0.01	2.29±0.00	-0.02±0.01
36 hours	- ± -	- ± -	3.30±0.01	+0.99±0.02	2.21±0.01	-0.10±0.02
6 months	1.87±0.11	-0.44±0.06 [†]	1.90±0.01	-0.41±0.02	- ± -	- ± -

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

† Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone III

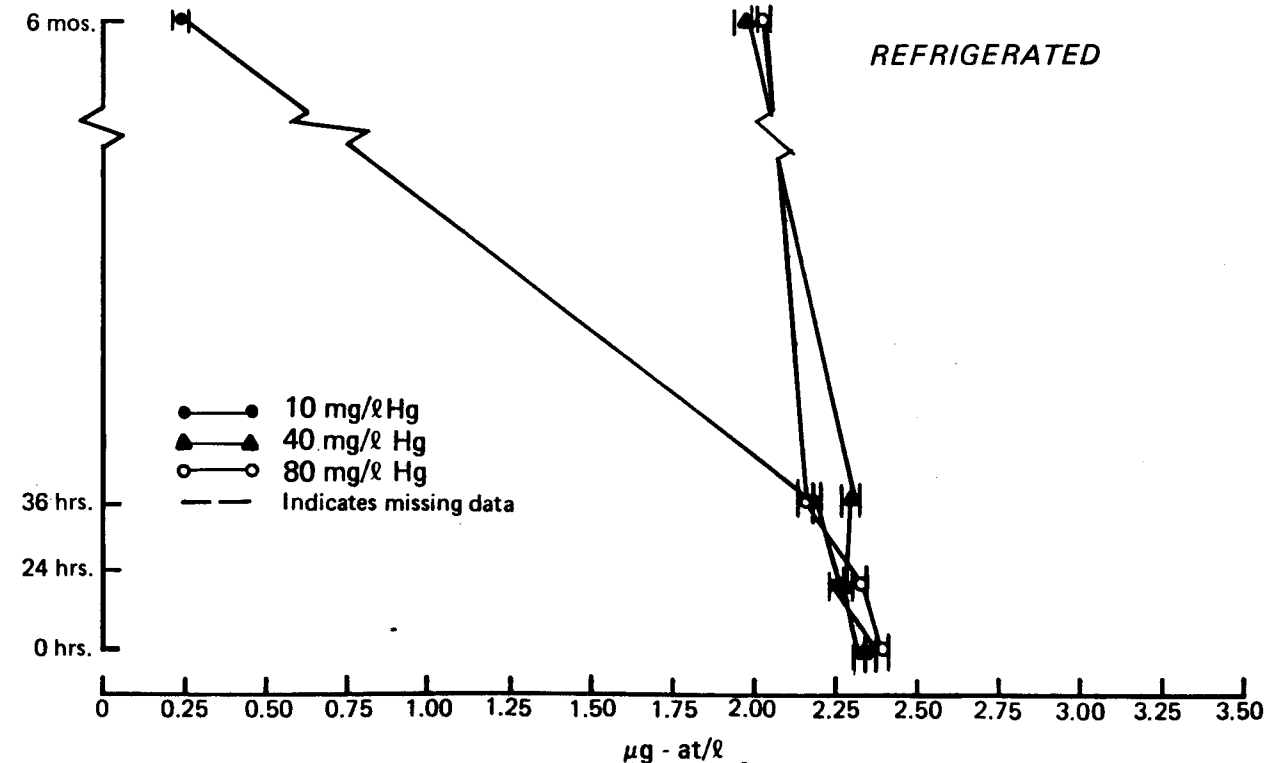
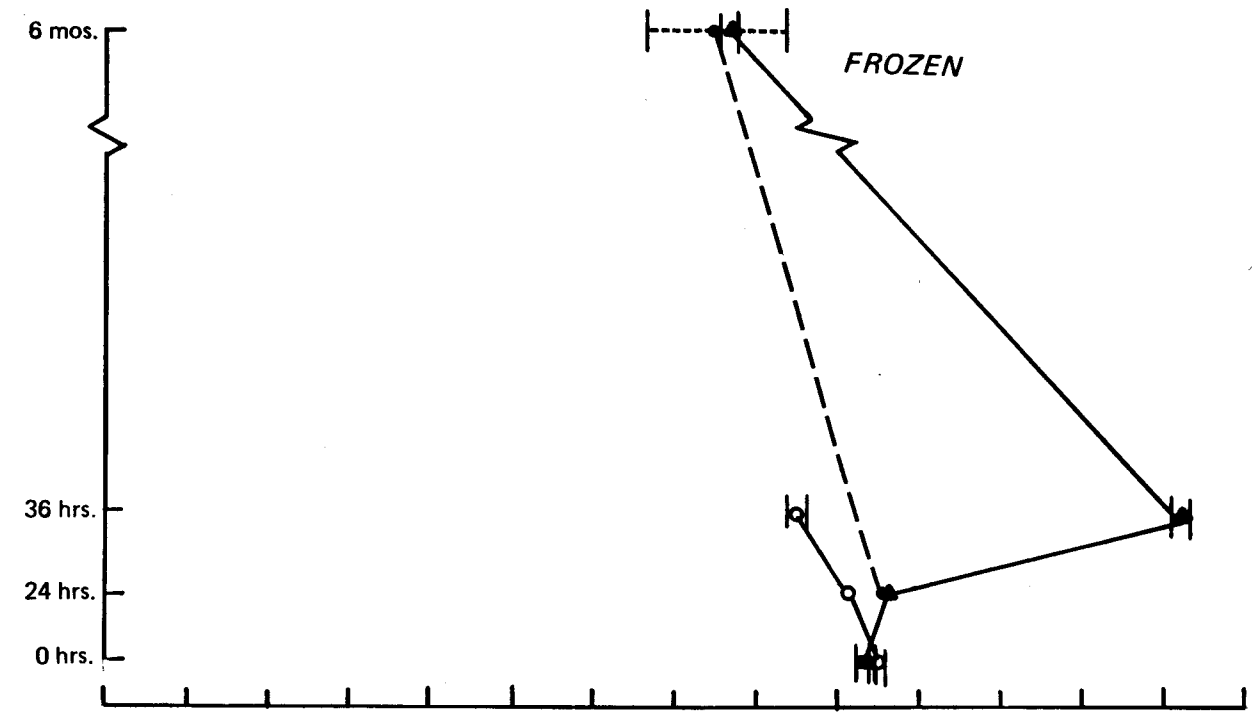


Figure 6. PO₄-P, Mean Zero Time, No Hg⁺² = 2.31±0.02 µg-at/l.

TABLE 7

Prince William Sound, Zone III.

Time of Analysis	NO ₃ -N, Mean Zero Time, No Hg ⁺² = 28.3±0.00 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	28.05±0.05	-0.25±0.04	28.05±0.05	-0.25±0.04	27.85±0.05	-0.45±0.04
24 hours	25.60±0.10	-2.70±0.07	25.50±0.20	-2.80±0.14	25.00±0.90	-3.30±0.64
36 hours	24.70±0.20	-3.60±0.14	25.20±0.10	-3.10±0.07	24.50±0.40	-3.80±0.28
6 months	23.90±0.40	-4.40±0.28	23.60±0.40	-4.70±0.28	23.55±0.15	-4.75±0.11
FROZEN						
0 hours	28.05±0.05	-0.25±0.04	28.05±0.05	-0.25±0.04	27.85±0.05	-0.45±0.04
24 hours	25.60±0.50	-2.70±0.35	24.60±0.10	-3.70±0.07	25.70±0.10	-2.60±0.07
36 hours	- ± -	- ± -	24.60±0.10	-3.70±0.07	25.00±0.10	-3.30±0.07
6 months	23.08±1.14	-5.22±0.57 [†]	23.75±0.35	-4.55±0.25	- ± -	- ± -

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Prince William Sound, Zone III

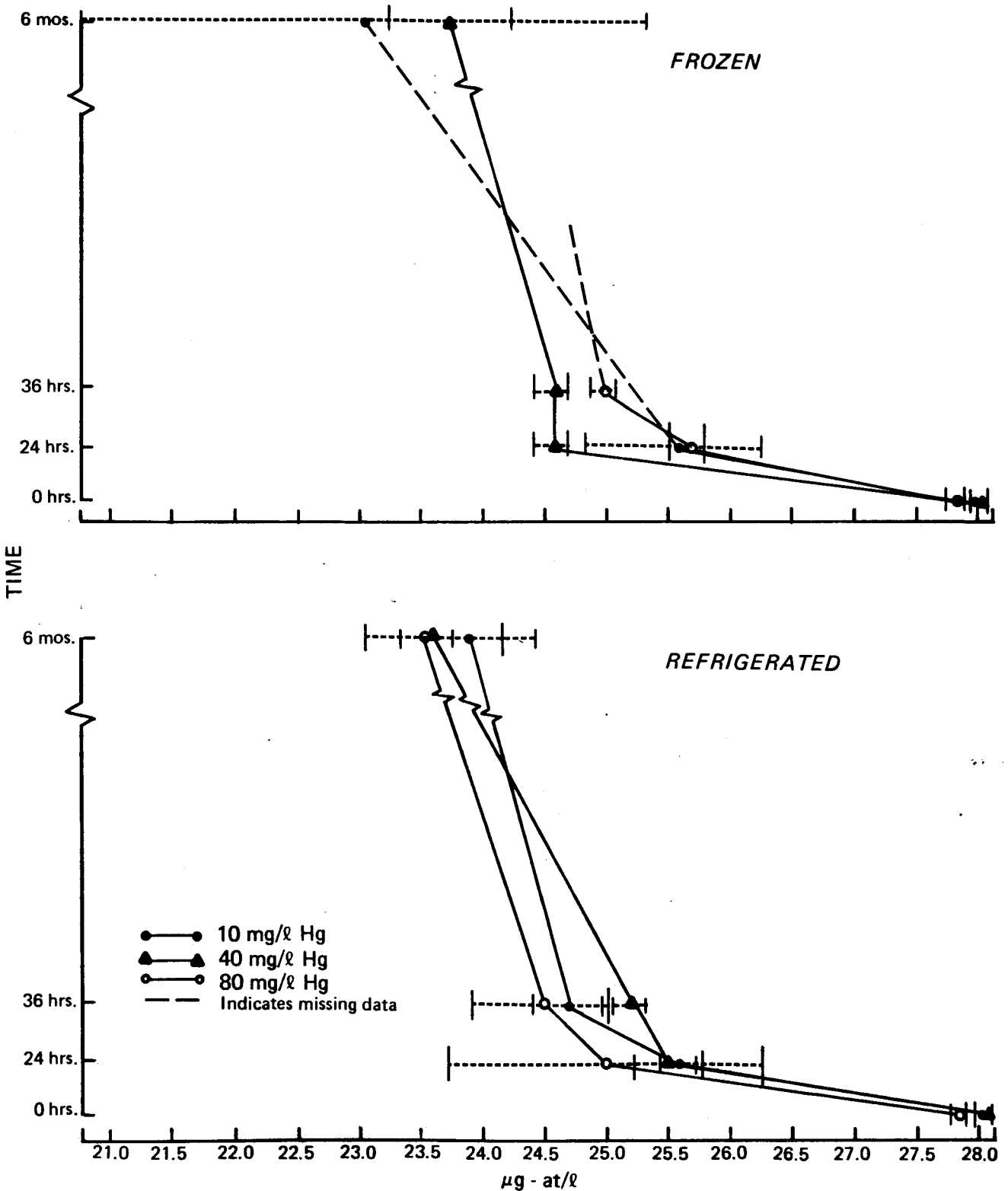


Figure 7. $\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 28.3 \pm 0.00 \mu\text{g-at}/\ell$.

TABLE 8

Gulf of Alaska, Zone I.

Time of Analysis	PO ₄ -P, Mean Zero Time, No Hg ⁺² = 0.65±0.01 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	0.65±0.03	0.00±0.02	0.43±0.01	-0.22±0.01	0.37±0.03	-0.28±0.02
24 hours	1.04±0.00	+0.39±0.01 [†]	0.97±0.07	+0.32±0.05	1.05±0.01	+0.40±0.01
36 hours	1.02±0.00	+0.37±0.01	1.02±0.00	+0.37±0.01	0.98±0.02	+0.33±0.02
6 months	1.07±0.01	+0.42±0.01	1.01±0.01	+0.36±0.01	1.01±0.01	+0.36±0.01
FROZEN						
0 hours	0.65±0.03	0.00±0.02	0.43±0.01	-0.22±0.01	0.37±0.03	-0.28±0.02
24 hours	1.00±0.00	+0.35±0.01	1.00±0.00	+0.35±0.01 ^{††}	0.96±0.00	+0.31±0.01
36 hours	0.98±0.00	+0.33±0.01	0.96±0.00	+0.31±0.01	0.98±0.00	+0.33±0.01
6 months	0.81±0.01	+0.16±0.01	0.83±0.01	+0.18±0.01	0.80±0.01	+0.15±0.01

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determinations - 3.

^{††} Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone I

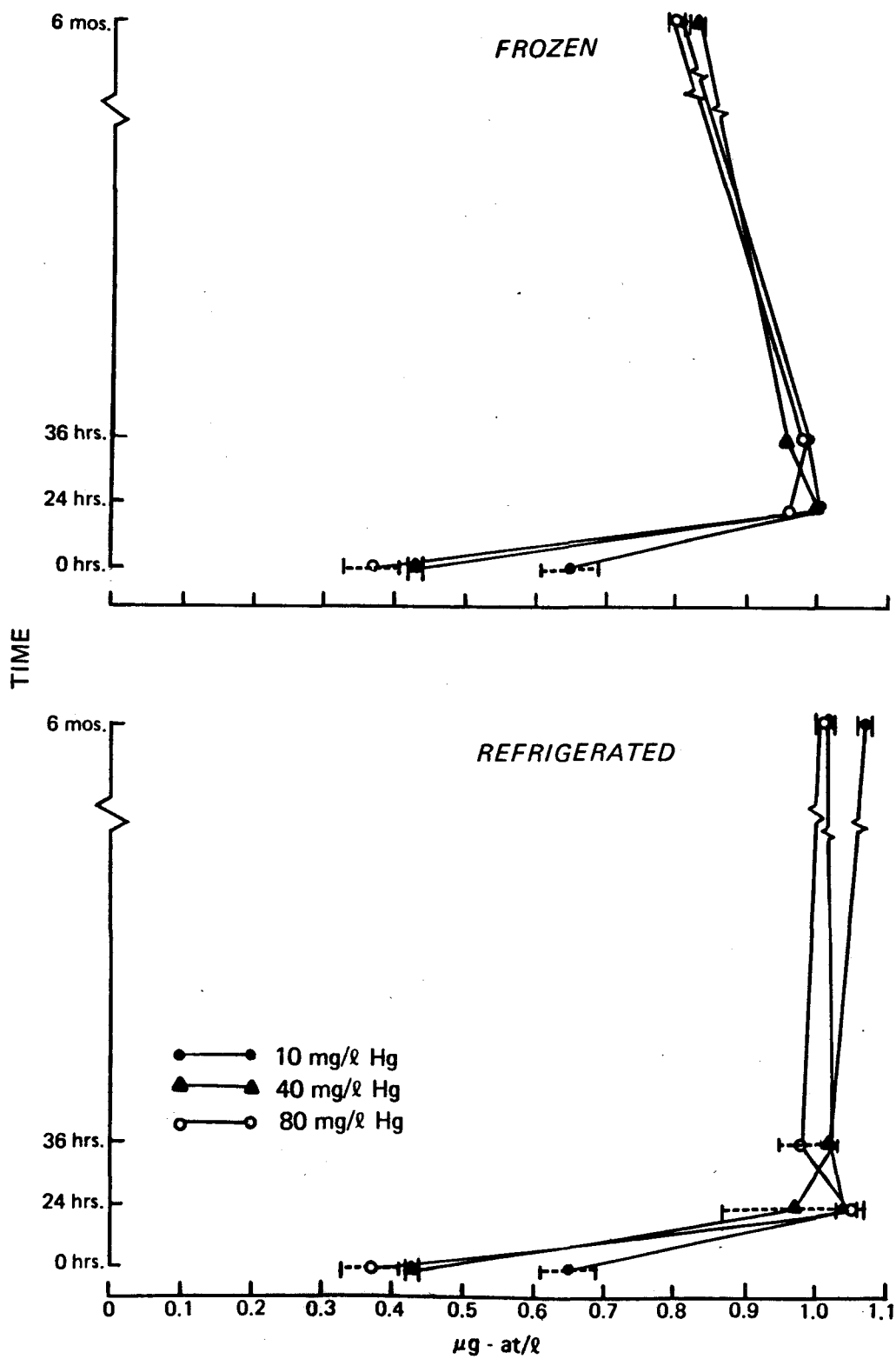


Figure 8. $\text{PO}_4\text{-P}$, Mean Zero Time, No $\text{Hg}^{+2} = 0.65 \pm 0.01 \mu\text{g-at/l}$.

TABLE 9

Gulf of Alaska, Zone I.

Time of Analysis	NO ₃ -N, Mean Zero Time, No Hg ⁺² = 8.58±0.16 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	8.16±0.04	-0.42±0.12	8.38±0.03	-0.20±0.12	8.48±0.00	-0.10±0.11
24 hours	8.88±0.04	+0.30±0.12	8.94±0.02	+0.36±0.11	8.23±0.19	-0.35±0.18
36 hours	8.51±0.01	-0.07±0.11	8.44±0.02	-0.14±0.11	8.04±0.37	-0.54±0.28
6 months	8.52±0.04	-0.06±0.12	8.27±0.04	-0.31±0.12	8.34±0.08	-0.24±0.13
FROZEN						
0 hours	8.16±0.04	-0.42±0.12	8.38±0.03	-0.20±0.12	8.48±0.00	-0.10±0.11
24 hours	9.30±0.06	+0.72±0.12	8.32±0.20	-0.26±0.18	8.92±0.02	+0.34±0.11
36 hours	8.56±0.06	-0.02±0.12	8.02±0.02	-0.56±0.11 [†]	8.29±0.18	-0.29±0.17
6 months	8.03±0.05	-0.55±0.12	8.09±0.06	-0.49±0.12	7.85±0.07	-0.73±0.12

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone I

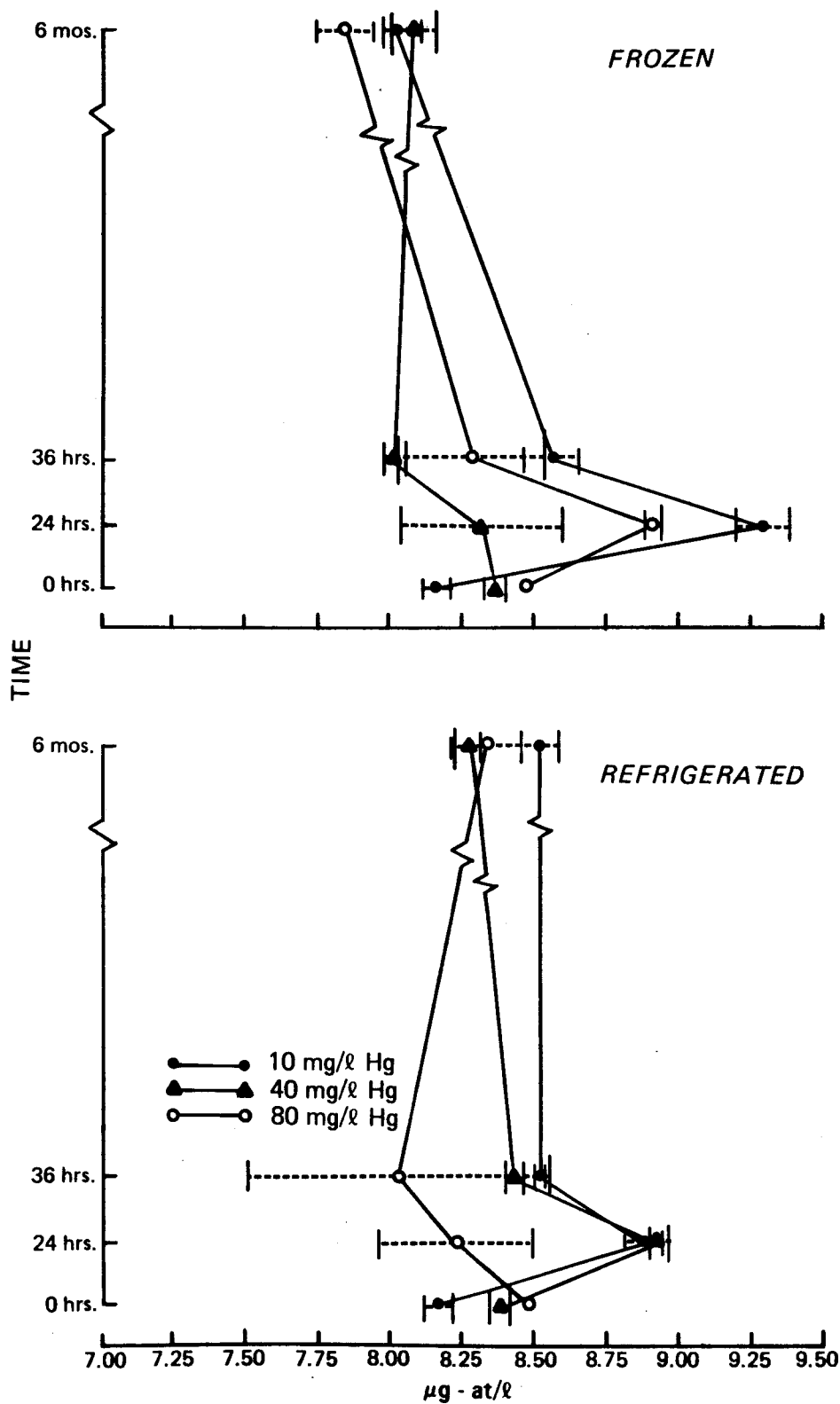


Figure 9. $\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 8.58 \pm 0.16 \mu\text{g-at/l}$.

TABLE 10

Gulf of Alaska, Zone II.

Time of Analysis	PO ₄ -P, Mean Zero Time, No Hg ⁺² = 1.26±0.06 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	1.33±0.03	+0.07±0.05 [†]	1.38±0.06	+0.12±0.06 [†]	1.29±0.02	+0.03±0.04
24 hours	1.76±0.03	+0.50±0.04 [†]	1.84±0.02	+0.58±0.04 [†]	1.86±0.01	+0.60±0.04
36 hours	1.76±0.04	+0.50±0.05	1.79±0.00	+0.53±0.04	1.75±0.00	+0.49±0.04
6 months	1.66±0.01	+0.40±0.04	1.76±0.01	+0.50±0.04	1.62±0.01	+0.36±0.04
FROZEN						
0 hours	1.33±0.03	+0.07±0.05	1.38±0.06	+0.12±0.06 [†]	1.29±0.02	+0.03±0.04
24 hours	2.06±0.10	+0.80±0.08	1.84±0.02	+0.58±0.04 [†]	1.82±0.01	+0.56±0.04
36 hours	1.79±0.00	+0.53±0.04	1.74±0.00	+0.48±0.04	1.74±0.00	+0.48±0.04
6 months	1.44±0.02	+0.18±0.04	1.54±0.01	+0.28±0.04	1.50±0.01	+0.24±0.04

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determinations - 4.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone II

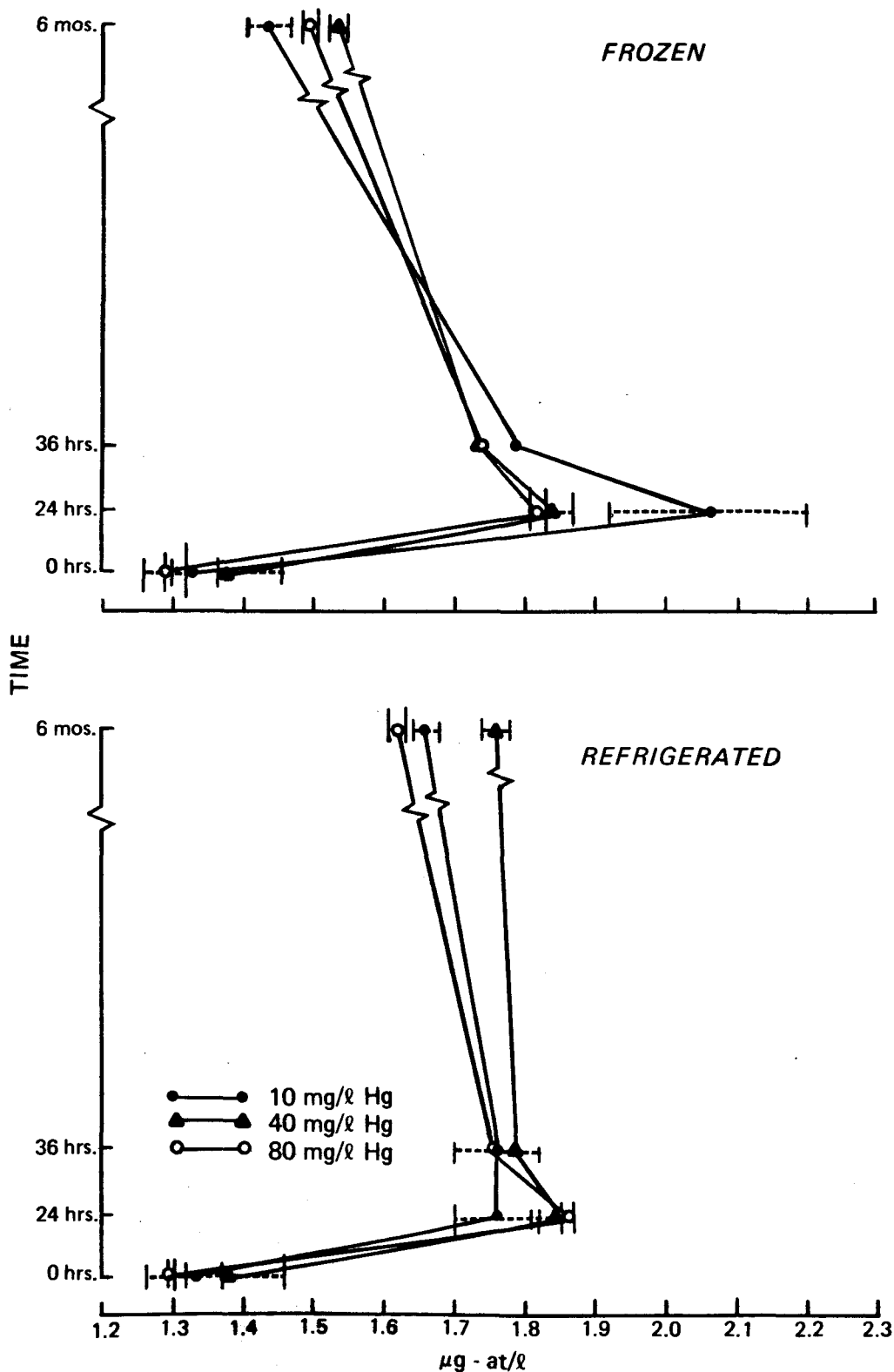


Figure 10. $\text{PO}_4\text{-P}$, Mean Zero Time, No $\text{Hg}^{+2} = 1.26 \pm 0.06 \mu\text{g-at}/\ell$.

TABLE 11

Gulf of Alaska, Zone II.

Time of Analysis	NO ₃ -N, Mean Zero Time, No Hg ⁺² = 19.70±0.10 µg-at/l					
	10 mg/l Hg ⁺²		40 mg/l Hg ⁺²		80 mg/l Hg ⁺²	
	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *	S	Δ±√v(Δ) *
REFRIGERATED						
0 hours	20.48±0.24	+0.78±0.14 [†]	20.37±0.27	+0.67±0.17 ^{††}	20.10±0.30	+0.40±0.22
24 hours	18.70±0.00	-1.00±0.07	20.82±0.34	+1.12±0.18 [†]	20.30±0.10	+0.60±0.10
36 hours	20.10±0.10	+0.40±0.10	20.00±0.00	+0.30±0.07	20.20±0.20	+0.50±0.16
6 months	19.55±0.15	-0.15±0.13	19.15±0.15	-0.55±0.13	19.05±0.05	-0.65±0.08
FROZEN						
0 hours	20.48±0.24	+0.78±0.14 [†]	20.37±0.27	+0.67±0.17 ^{††}	20.10±0.30	+0.40±0.22
24 hours	20.40±0.60	+0.70±0.43	20.75±0.39	+1.05±0.21 [†]	20.90±0.50	+1.20±0.36
36 hours	20.00±0.20	+0.30±0.16	20.05±0.24	+0.35±0.18	20.10±0.10	+0.40±0.10
6 months	18.10±0.30	-1.60±0.22	19.15±0.05	-0.55±0.08	18.70±0.30	-1.00±0.22

* Δ change in relationship to mean zero time concentration which contained no Hg⁺².

[†] Number of determinations - 4.

^{††} Number of determinations - 3.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone II

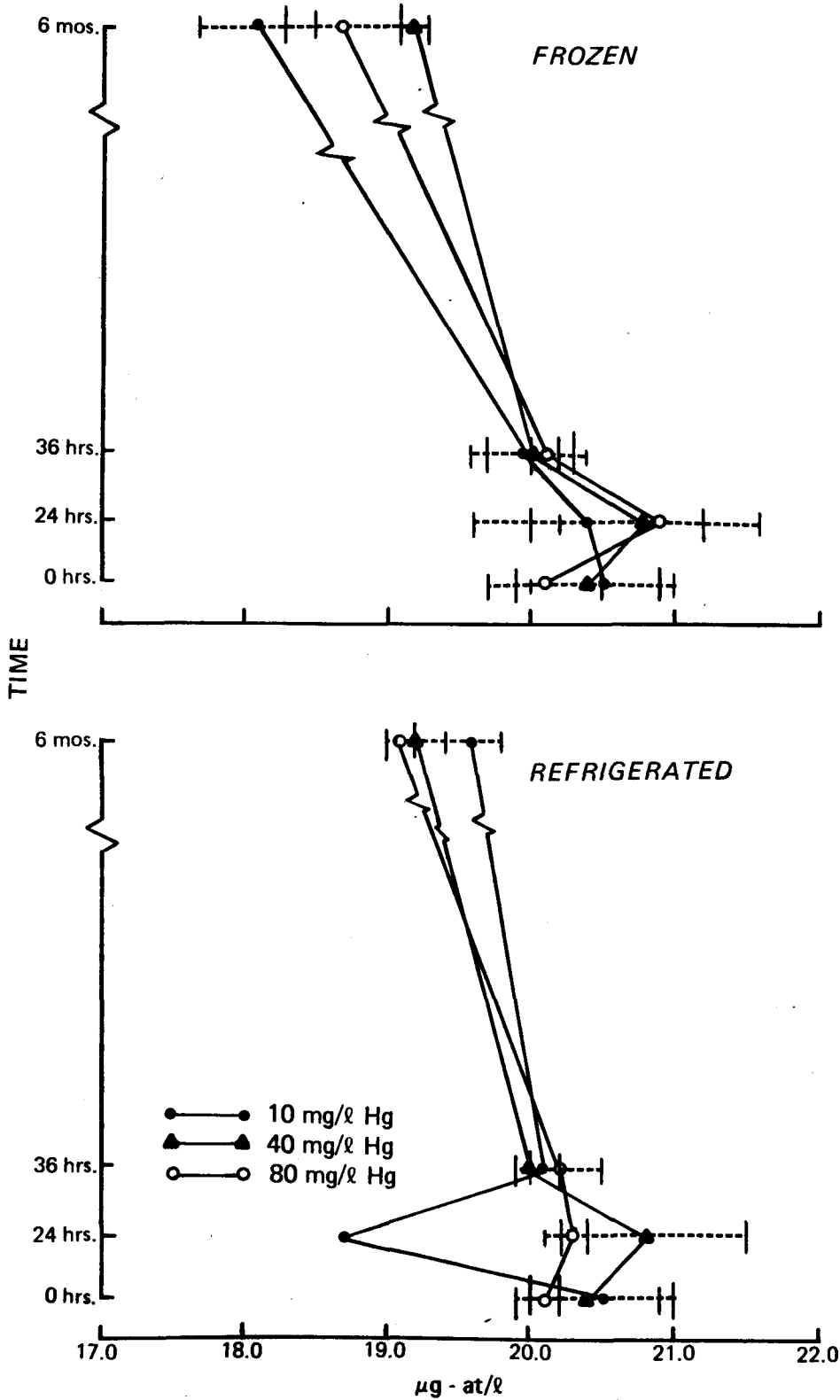


Figure 11. $\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 19.70 \pm 0.10 \mu\text{g-at}/\ell$.

TABLE 12

Gulf of Alaska, Zone III.

Time of Analysis	$\text{PO}_4\text{-P}$, Mean Zero Time, No $\text{Hg}^{+2} = 2.62 \pm 0.15 \text{ } \mu\text{g-at}/\ell$					
	10 mg/ ℓ Hg^{+2}		40 mg/ ℓ Hg^{+2}		80 mg/ ℓ Hg^{+2}	
	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *
REFRIGERATED						
0 hours	2.92 \pm 0.06	+0.30 \pm 0.11	3.13 \pm 0.05	+0.51 \pm 0.11 [†]	3.48 \pm 0.10	+0.86 \pm 0.12 [†]
24 hours	3.92 \pm 0.00	+1.30 \pm 0.11	3.68 \pm 0.01	+1.06 \pm 0.11	3.92 \pm 0.00	+1.30 \pm 0.11
36 hours	3.25 \pm 0.00	+0.63 \pm 0.11	3.34 \pm 0.02	+0.72 \pm 0.11	3.32 \pm -	+0.70 \pm -
6 months	3.47 \pm 0.02	+0.85 \pm 0.11	3.02 \pm 0.01	+0.40 \pm 0.11	3.36 \pm 0.01	+0.74 \pm 0.11
FROZEN						
0 hours	2.92 \pm 0.06	+0.30 \pm 0.11	3.13 \pm 0.05	+0.51 \pm 0.11 [†]	3.48 \pm 0.10	+0.86 \pm 0.12 [†]
24 hours	3.92 \pm 0.00	+1.30 \pm 0.11	3.72 \pm 0.06	+1.10 \pm 0.11 ^{††}	3.64 \pm 0.01	+1.02 \pm 0.11
36 hours	3.36 \pm -	+0.74 \pm -	3.12 \pm -	+0.50 \pm -	3.62 \pm 0.21	+1.00 \pm 0.18
6 months	2.96 \pm 0.01	+0.34 \pm 0.11	2.36 \pm 0.08	-0.26 \pm 0.12	3.01 \pm 0.02	+0.39 \pm 0.11

* Δ change in relationship to mean zero time concentration which contained no Hg^{+2} .

[†] Number of determinations - 3.

^{††} Number of determinations - 1.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone III

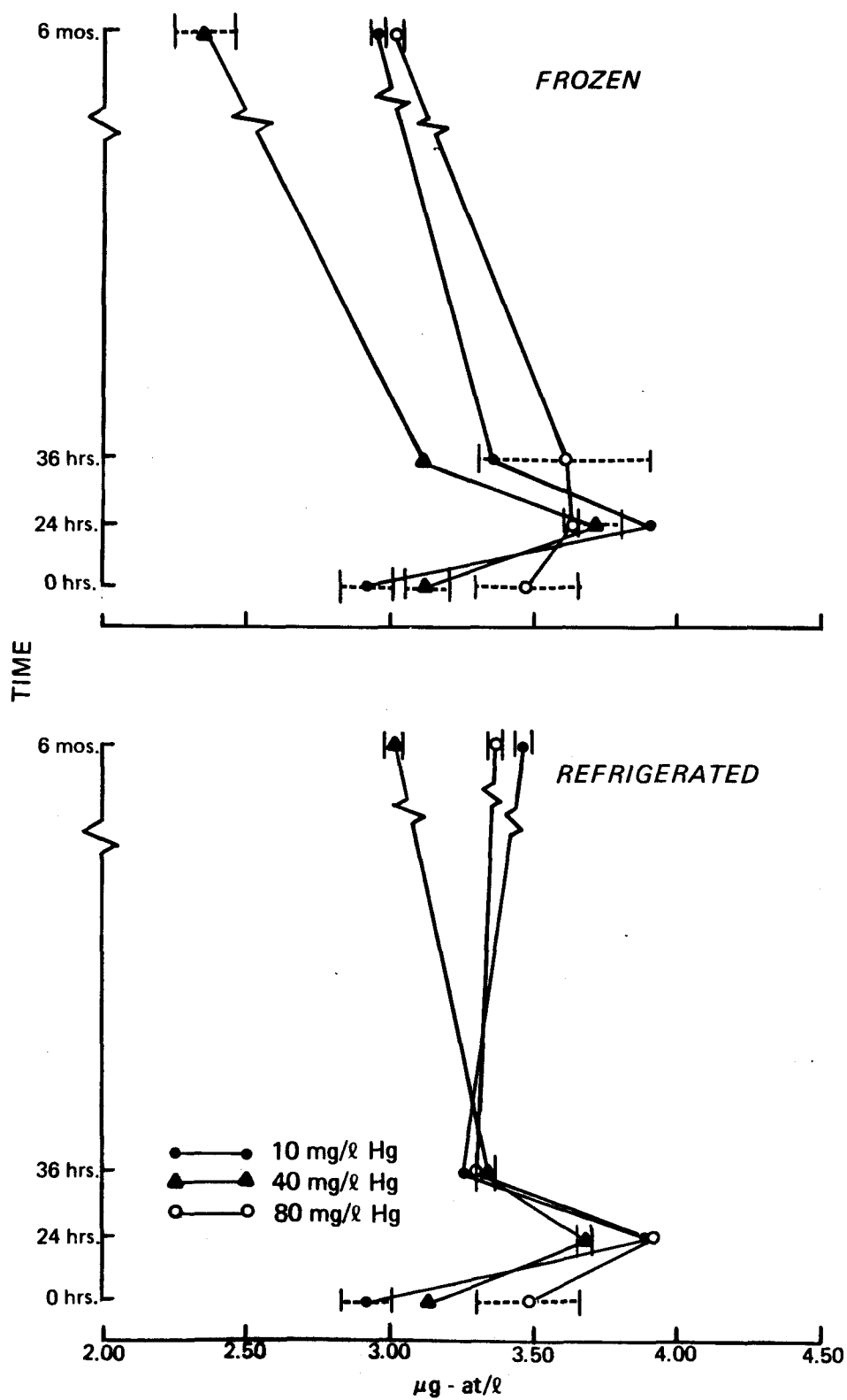


Figure 12. $\text{PO}_4\text{-P}$, Mean Zero Time, No $\text{Hg}^{+2} = 2.62 \pm 0.15 \mu\text{g-at}/\ell$.

TABLE 13

Gulf of Alaska, Zone III.

Time of Analysis	$\text{NO}_3\text{-N}$, Mean Zero Time, No $\text{Hg}^{+2} = 47.10 \pm - \mu\text{g-at}/\ell^{++}$					
	10 mg/l Hg^{+2}		40 mg/l Hg^{+2}		80 mg/l Hg^{+2}	
	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *	S	$\Delta \pm \sqrt{v(\Delta)}$ *
REFRIGERATED						
0 hours	46.10± -	-1.00± - †	45.70± -	-1.40± - †	46.10± -	-1.00± - †
24 hours	42.80±0.10	-4.30± - †	45.90± -	-1.20± - †	42.75±0.85	-4.35± -
36 hours	43.60± -	-3.50± - †	42.80±0.80	-4.30± -	42.80±0.40	-4.30± -
6 months	45.85±0.25	-1.25± -	42.20±0.10	-4.90± -	45.45±0.35	-1.65± -
FROZEN						
0 hours	46.10± -	-1.00± - †	45.70± -	-1.40± - †	46.10± -	-1.00± - †
24 hours	41.75±0.95	-5.35± -	42.70± -	-4.40± - †	41.90± -	-5.20± - †
36 hours	41.85±0.95	-5.25± - †	42.60± -	-4.50± - †	42.50±0.10	-4.60± -
6 months	41.80± -	-5.30± - †	42.80± -	-4.30± - †	44.30±0.10	-2.80± -

* Δ change in relationship to mean zero time concentration which contained no Hg^{+2} .

† Number of determinations - 1.

S = Standard error of the mean.

v = Variation.

Gulf of Alaska, Zone III

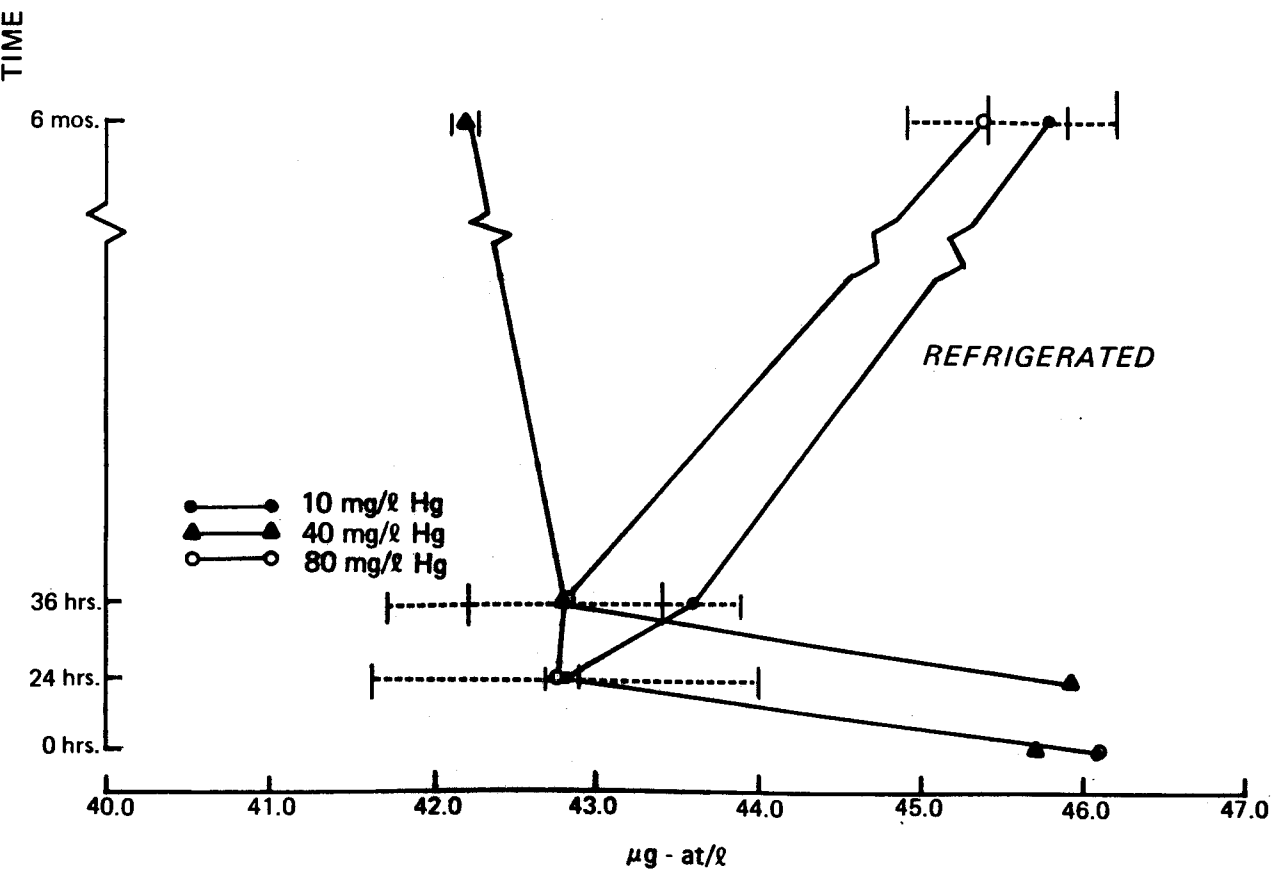
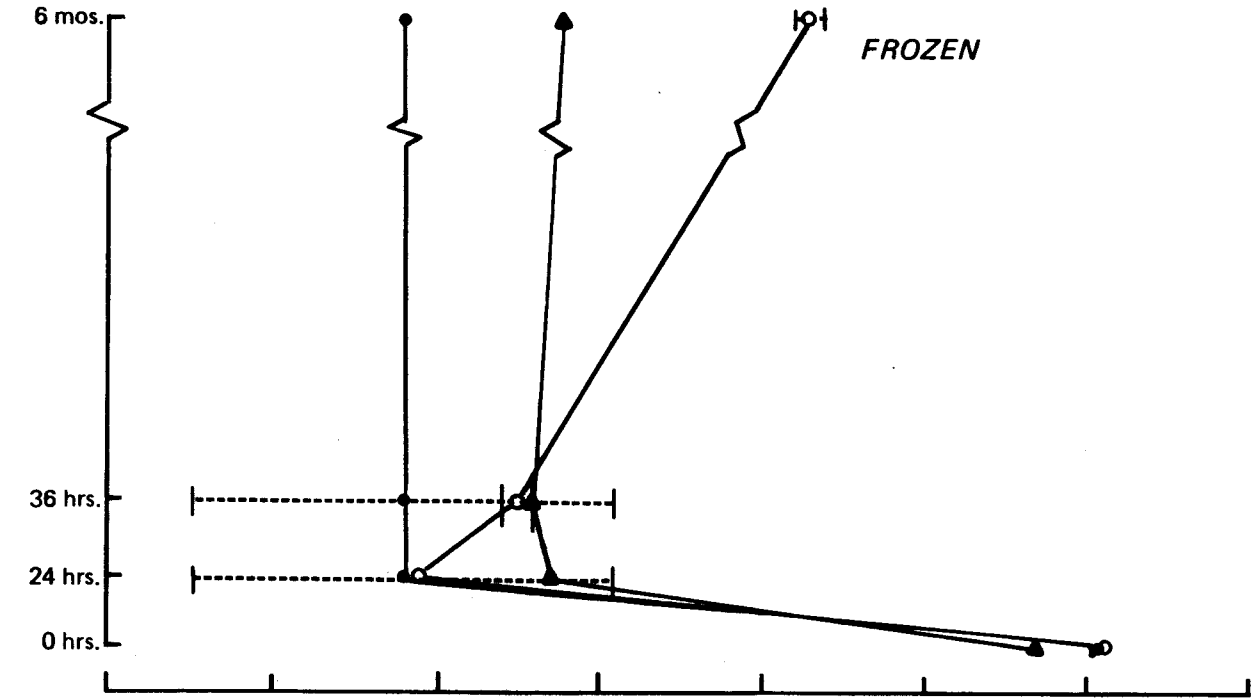


Figure 13. $\text{NO}_3\text{-N}$, Mean Zero Time, $\text{No Hg}^{+2} = 47.10 \pm \mu\text{g-at/l}$.

TABLE 14

Standards - Least square analysis (BMD05R).

Number of Standards	Range Concentration ($\mu\text{g-at/l}$)	Concentration(x) Intercept	Correlation Coefficient
<u>NO₃-N</u>			
For 0, 24, 36 hours analysis			
84	0.5 - 15.0	-0.00014	0.99719
For 6 months analysis			
26	0.5 - 15.0	-0.00729	0.99531
<u>PO₄-P</u>			
For 0, 24, 36 hours analysis			
79	0.50 - 3.50	-0.00220	0.99901
For 6 months analysis			
30	0.50 - 3.50	-0.00115	0.99796

APPENDIX I

The following variables are used to compute the Statistical Analysis of Variance in Appendix I. Concentration of $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ for:

Time 1 - zero time

Time 2 - 24 hours

Time 3 - 36 hours

Time 4 - 6 months

Hg 1 - 10 mg/l Hg^{+2}

Hg 2 - 40 mg/l Hg^{+2}

Hg 3 - 80 mg/l Hg^{+2}

Temp 1 - refrigerated

Temp 2 - frozen

APPENDIX I

Analysis of Variance Table ($\alpha = 0.05$)

Prince William Sound - Zone I					PO ₄ -P	
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value	
Mean	20.715	1	20.715	115943.88	-	
Time	0.020	3	0.007	38.89	2.99	
Hg	0.001	2	0.001	4.06	3.39	
Temp	0.014	1	0.014	80.81	4.24	
Time Hg	0.005	6	0.001	4.78	2.49	
Time Temp	0.007	3	0.002	12.54	2.99	
Hg Temp	0.004	2	0.002	12.07	3.39	
Hg Tim/Temp	0.007	6	0.001	6.95	2.49	
Time 12	0.003	1	0.003	17.92	4.24	
Time 13	0.000	1	0.000	0.84	4.24	
Time 14	0.007	1	0.007	41.14	4.24	
Time 23	0.005	1	0.005	26.65	4.24	
Time 24	0.021	1	0.021	115.31	4.24	
Time 34	0.005	1	0.005	30.22	4.24	
Hg 12	0.000	1	0.000	2.12	4.24	
Hg 13	0.001	1	0.001	3.56	4.24	
Hg 23	0.000	1	0.000	1.91	4.24	
Temp 12	0.014	1	0.014	80.81	4.24	
Error	0.004	25	0.000	-	-	

					NO ₃ -N	
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value	
Mean	1430.440	1	1430.440	27528.23	-	
Time	4.599	3	1.533	29.50	2.99	
Hg	0.054	2	0.027	0.52	3.39	
Temp	0.087	1	0.087	1.68	4.24	
Time Hg	0.619	6	0.103	1.98	2.49	
Time Temp	0.077	3	0.026	0.49	2.99	
Hg Temp	0.317	2	0.158	3.05	3.39	
Hg Tim/Temp	0.477	6	0.080	1.53	2.49	
Time 12	4.297	1	4.297	82.70	4.24	
Time 13	0.944	1	0.944	18.17	4.24	
Time 14	0.341	1	0.341	6.56	4.24	
Time 23	1.183	1	1.183	22.76	4.24	
Time 24	2.193	1	2.193	42.20	4.24	
Time 34	0.150	1	0.150	2.89	4.24	
Error	1.299	25	0.052	-	-	

APPENDIX I (Continued)

Prince William Sound - Zone II					PO ₄ -P
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	107.988	1	107.988	8053.41	-
Time	2.563	3	0.854	63.72	2.95
Hg	0.344	2	0.172	12.82	3.34
Temp	0.022	1	0.022	1.65	4.20
Time Hg	1.257	6	0.210	15.63	2.45
Time Temp	0.040	3	0.013	0.98	2.95
Hg Temp	0.056	2	0.028	2.09	3.34
Hg Tim/Temp	0.051	6	0.009	0.64	2.45
Time 12	2.053	1	2.053	153.13	4.20
Time 13	1.654	1	1.654	123.33	4.20
Time 14	0.525	1	0.525	39.19	4.20
Time 23	0.022	1	0.022	1.61	4.20
Time 24	0.596	1	0.596	44.42	4.20
Time 34	0.382	1	0.382	28.51	4.20
Hg 12	0.002	1	0.002	0.18	4.20
Hg 13	0.024	1	0.024	1.78	4.20
Hg 23	0.225	1	0.225	16.80	4.20
Temp 12	0.022	1	0.022	1.65	4.20
Error	0.375	28	0.013	1.65	-

					NO ₃ -N
Mean	15297.159	1	15297.156	29023.91	-
Time	43.218	3	14.406	27.33	2.95
Hg	4.413	2	2.207	4.19	3.34
Temp	1.174	1	1.174	2.23	4.20
Time Hg	7.733	6	1.289	2.44	2.45
Time Temp	2.382	3	0.794	1.51	2.95
Hg Temp	1.024	2	0.512	0.97	3.34
Hg Tim/Temp	2.927	6	0.488	0.93	2.45
Time 12	14.727	1	14.727	27.94	4.20
Time 13	12.327	1	12.327	23.39	4.20
Time 14	42.980	1	42.980	81.55	4.20
Time 23	0.107	1	0.107	0.20	4.20
Time 24	6.491	1	6.491	12.32	4.20
Time 34	8.346	1	8.346	15.83	4.20
Hg 12	3.728	1	3.728	7.07	4.20
Hg 13	3.037	1	3.037	5.76	4.20
Hg 23	2.791	1	2.791	5.30	4.20
Temp 12	1.174	1	1.174	2.23	4.20
Error	14.758	28	0.527	-	-

APPENDIX I (Continued)

Prince William Sound - Zone III					PO ₄ -P
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	220.854	1	220.854	34975.30	-
Time	7.893	3	2.631	416.66	3.01
Hg	0.578	2	0.289	45.76	3.40
Temp	0.680	1	0.680	107.72	4.26
Time Hg	1.973	6	0.329	52.08	2.51
Time Temp	1.401	3	0.467	73.95	3.01
Hg Temp	2.108	2	1.054	166.94	3.40
Hg Tim/Temp	2.313	6	0.385	61.04	2.51
Time 12	0.000	1	0.000	0.02	4.26
Time 13	0.567	1	0.567	89.81	4.26
Time 14	3.944	1	3.944	624.62	4.26
Time 23	0.550	1	0.550	87.03	4.26
Time 24	3.992	1	3.992	632.19	4.26
Time 34	7.023	1	7.023	1112.14	4.26
Hg 12	0.170	1	0.170	26.96	4.26
Hg 13	0.079	1	0.079	12.51	4.26
Hg 23	0.575	1	0.575	91.00	4.26
Temp 12	0.680	1	0.680	107.72	4.26
Error	0.152	24	0.006	-	-

					NO ₃ -N
Mean	31712.228	1	31712.227	42473.57	-
Time	127.564	3	42.522	56.95	2.98
Hg	0.156	2	0.078	0.10	3.37
Temp	0.028	1	0.028	0.04	4.23
Time Hg	0.725	6	0.121	0.16	2.47
Time Temp	0.176	3	0.059	0.08	2.98
Hg Temp	0.834	2	0.417	0.56	3.37
Hg Tim/Temp	1.828	6	0.305	0.41	2.47
Time 12	42.135	1	42.135	56.43	4.23
Time 13	58.907	1	58.907	78.90	4.23
Time 14	121.900	1	121.900	163.27	4.23
Time 23	1.402	1	1.402	1.88	4.23
Time 24	19.449	1	19.449	26.05	4.23
Time 34	10.244	1	10.244	13.72	4.23
Error	19.412	26	0.747	-	-

APPENDIX I (Continued)

Gulf of Alaska - Zone I					PO ₄ -P
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	35.904	1	35.904	33466.32	-
Time	2.231	3	0.744	693.24	2.96
Hg	0.071	2	0.035	33.05	3.35
Temp	0.063	1	0.063	58.60	4.21
Time Hg	0.111	6	0.018	17.25	2.46
Time Temp	0.088	3	0.029	27.23	2.96
Hg Temp	0.002	2	0.001	1.12	3.35
Hg Tim/Temp	0.011	6	0.002	1.67	2.46
Time 12	1.672	1	1.672	1558.78	4.21
Time 13	1.607	1	1.607	1498.11	4.21
Time 14	1.153	1	1.153	1074.55	4.21
Time 23	0.001	1	0.001	1.16	4.21
Time 24	0.042	1	0.042	38.89	4.21
Time 34	0.029	1	0.029	27.25	4.21
Hg 12	0.040	1	0.040	37.54	4.21
Hg 13	0.053	1	0.053	49.19	4.21
Hg 23	0.003	1	0.003	2.52	4.21
Temp 12	0.063	1	0.063	58.60	4.21
Error	0.029	27	0.001	-	-

					NO ₃ -N
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	3459.199	1	3459.198	132531.44	-
Time	2.292	3	0.764	29.27	2.98
Hg	0.334	2	0.167	6.39	3.37
Temp	0.053	1	0.053	2.05	4.23
Time Hg	0.896	6	0.149	5.72	2.47
Time Temp	0.486	3	0.162	6.21	2.98
Hg Temp	0.376	2	0.188	7.21	3.37
Hg Tim/Temp	0.893	6	0.149	5.70	2.47
Time 12	1.071	1	1.071	41.03	4.23
Time 13	0.006	1	0.006	0.23	4.23
Time 14	0.147	1	0.147	5.64	4.23
Time 23	1.289	1	1.289	49.39	4.23
Time 24	2.013	1	2.013	77.11	4.23
Time 34	0.098	1	0.098	3.77	4.23
Hg 12	0.206	1	0.206	7.91	4.23
Hg 13	0.263	1	0.263	10.06	4.23
Hg 23	0.006	1	0.006	0.22	4.23
Temp 12	0.053	1	0.053	2.05	4.23
Error	0.679	26	0.026	-	-

APPENDIX I (Continued)

Gulf of Alaska - Zone II					PO ₄ -P	
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value	
Mean	137.484	1	137.484	70909.12	-	
Time	2.160	3	0.720	371.33	2.91	
Hg	0.022	2	0.011	5.67	3.31	
Temp	0.010	1	0.010	5.03	4.16	
Time Hg	0.042	6	0.007	3.57	2.41	
Time Temp	0.133	3	0.044	22.79	2.91	
Hg Temp	0.020	2	0.010	5.27	3.31	
Hg Tim/Temp	0.066	6	0.011	5.65	2.41	
Time 12	1.951	1	1.951	1006.48	4.16	
Time 13	1.114	1	1.114	574.41	4.16	
Time 14	0.380	1	0.380	196.00	4.16	
Time 23	0.069	1	0.069	35.77	4.16	
Time 24	0.540	1	0.540	278.44	4.16	
Time 34	0.193	1	0.193	99.34	4.16	
Hg 12	0.002	1	0.002	1.04	4.16	
Hg 13	0.000	1	0.000	0.14	4.16	
Hg 23	0.021	1	0.021	10.97	4.16	
Temp 12	0.010	1	0.010	5.03	4.16	
Error	0.060	31	0.002	-	-	

					NO ₃ -N	
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value	
Mean	21412.160	1	21412.160	92495.06	-	
Time	16.269	3	5.423	23.43	2.89	
Hg	1.229	2	0.615	2.66	3.28	
Temp	0.007	1	0.007	0.03	4.13	
Time Hg	3.790	6	0.632	2.73	2.39	
Time Temp	3.030	3	1.010	4.36	2.89	
Hg Temp	0.006	2	0.003	0.01	3.28	
Hg Tim/Temp	3.183	6	0.530	2.29	2.39	
Time 12	0.000	1	0.000	0.00	4.13	
Time 13	0.398	1	0.398	1.72	4.13	
Time 14	12.961	1	12.961	55.99	4.13	
Time 23	0.369	1	0.369	1.60	4.13	
Time 24	12.151	1	12.151	52.49	4.13	
Time 34	7.594	1	7.594	32.80	4.13	
Error	7.871	34	0.232	-	-	

APPENDIX I (Continued)

Gulf of Alaska - Zone III					PO ₄ -P
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	499.366	1	499.366	44249.16	-
Time	4.068	3	1.356	120.16	2.99
Hg	0.659	2	0.329	29.19	3.39
Temp	0.192	1	0.192	17.02	4.24
Time Hg	0.914	6	0.152	13.50	2.49
Time Temp	0.563	3	0.188	16.63	2.99
Hg Temp	0.035	2	0.018	1.55	3.39
Hg Tim/Temp	0.176	6	0.029	2.60	2.49
Time 12	2.611	1	2.611	231.36	4.24
Time 13	0.130	1	0.130	11.50	4.24
Time 14	0.143	1	0.143	12.67	4.24
Time 23	1.038	1	1.038	91.97	4.24
Time 24	3.534	1	3.534	313.18	4.24
Time 34	0.439	1	0.439	38.92	4.24
Hg 12	0.179	1	0.179	15.89	4.24
Hg 13	0.083	1	0.083	7.32	4.24
Hg 23	0.658	1	0.658	58.31	4.24
Temp 12	0.192	1	0.192	17.02	4.24
Error	0.282	25	0.011	-	-

					NO ₃ -N
Source	Sum of Squares	D.F.	Mean Square	F	Critical Value
Mean	59838.898	1	59838.898	92642.88	-
Time	44.256	3	14.752	22.84	3.59
Hg	0.393	2	0.196	0.30	3.98
Temp	7.719	1	7.719	11.95	4.84
Time Hg	14.375	6	2.396	3.71	3.09
Time Temp	3.224	3	1.075	1.66	3.59
Hg Temp	2.085	2	1.042	1.61	3.98
Hg Tim/Temp	8.217	6	1.370	2.12	3.09
Time 12	30.857	1	30.857	47.77	4.84
Time 13	38.612	1	38.612	59.78	4.84
Time 14	17.956	1	17.956	27.80	4.84
Time 23	0.320	1	0.320	0.50	4.84
Time 24	2.489	1	2.489	3.85	4.84
Time 34	4.883	1	4.883	7.56	4.84
Hg 12	0.023	1	0.023	0.04	4.84
Hg 13	0.068	1	0.068	0.10	4.84
Hg 23	0.180	1	0.180	0.28	4.84
Temp 12	7.719	1	7.719	11.95	4.84
Error	7.105	11	0.646	-	-

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