NOAA Technical Memorandum NMFS-F/NEC-53

Contaminants in Hudson-Raritan Estuary Water and Influence of Cold Storage upon its Chemical Composition

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
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Northeast Fisheries Center
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The editors wish to thank those individuals who were provided a contract by the National Marine Fisheries Serivce to perform the chemical analyses and to provide summary reports included in this document:

- Chlorinated hydrocarbons; A. G. Requejo, J. Brown, and S. Duffy, Battelle New England Marine Research Laboratory, Duxbury, Massachusetts

- Polynuclear aromatics and other petroleum hydrocarbons; J. N. Gearing and P. J. Gearing, Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island

- Trace metals; D. Cullen, P. Heggie, and P. Joyce, Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island

ABSTRACT

NOAA's Ocean Assessments Division initiated a study through the Milford, Connecticut and Narragansett, Rhode Island, laboratories of the National Marine Fisheries Service to determine the influence of Hudson-Raritan Estuary water quality on the early development of finfish, molluscs, and crustaceans. As part of the study, detailed chemical analyses were conducted to determine the levels of the major classes of contaminants in the Hudson-Raritan Estuary, and to determine whether refrigerated storage of this water would induce significant changes in chemical composition.

Concentrations of selected chlorinated hydrocarbons, petroleum hydrocarbons, and trace metals were measured in initial water samples and monitored over two- and three-week periods of refrigerated storage. Of the chlorinated hydrocarbons selected, only polychlorinated biphenyls (PCBs) were detected in significant quantities. Average total PCB concentrations in seasonal samples ranged between 5.5 and 19.5 ng/l and exhibited no analytically significant change in concentration during refrigerated storage. Dissolved PCBs accounted for the major portion of total concentrations, with particulate PCBs comprising only 23-28% of the total.

Levels of total high molecular weight petroleum hydrocarbons ranged from 32 ug/l to 84 ug/l. Polynuclear aromatics made up 36-46% of the total hydrocarbons measured. Up to 70% of the the hydrocarbons were associated with particulate material. The concentrations of total hydrocarbons did not change during three weeks of storage.

Of the metals tested, cadmium and copper increased in concentration during refrigerated storage of the water samples, whereas manganese and nickel concentrations remained constant. Due to contamination problems and the variability encountered with measurements of iron, it was difficult to assess the effect of refrigerated storage on this metal. Lead concentrations were below the level of detection.

BIBLIOGRAPHIC INFORMATION

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Abstract: A study assessed the inputs of pollutants from various sources, including river waters and resuspended sediment, municipal wastewater effluents, and raw and treated sewage discharges. The report describes the results of laboratory experiments that monitored levels of selected chlorinated hydrocarbons, trace metals, and petroleum hydrocarbons at regular intervals.

1. INTRODUCTION

Inputs of pollutants to the Hudson-Raritan Estuary originate from a variety of sources, including contaminated Hudson River waters and resuspended sediment, municipal wastewater effluents, and both raw and treated sewage discharges (Bopp et al., 1981, 1982; O'Connor et al., 1982; Boehm, 1983). These combined inputs can result in elevated levels of pollutants in estuary waters which might impair the reproductive and developmental abilities of resident fish and shellfish. To examine the significance of this potential ecological impact, NOAA's Ocean Assessments Division initiated a study through the Milford, Connecticut, and Narragansett, Rhode Island, laboratories of the National Marine Fisheries Service to test the hypothesis that the reproductive capacity of fish and shellfish might be impaired by the levels of pollutants found in waters of the Hudson-Raritan Estuary.

As a part of the initial feasibility stages of the study, detailed chemical analyses were conducted to determine the levels of the major classes of contaminants, including petroleum hydrocarbons, chlorinated hydrocarbons [polychlorinated biphenyls (PCBs), DDT isomers], and trace metals in the Hudson-Raritan Estuary, and to determine whether large volume samples of this water could be transported to the laboratory and held in refrigerated storage prior to initiating biological assays without significant changes in contaminant composition or amounts. This report describes the results of laboratory experiments in which concentrations of selected chlorinated hydrocarbons, trace metals, and petroleum hydrocarbons in samples of Hudson-Raritan Estuary water were monitored at regular intervals during two- and three-week periods of refrigerated storage.

The chemical analyses were performed with contracts to the University of Rhode Island (trace metals and petroleum hydrocarbons) and the Battelle New England Marine Research Laboratory (chlorinated hydrocarbons).

2. WATER COLLECTION

Because of the variety of chemical analyses to be made in this study, it was difficult to choose a proper container for the collection and storage of the water to be analyzed. After due consideration, it was decided that clear-glass 20-l spring water carboys would have the least effect on the chemical analyses of concern. The carboys used were fairly old (up to 40 years) and well-seasoned.

Prior to water collection, all carboys were prepared according to a protocol established for the different chemical analyses. For metals analyses, carboys were first washed with Alconox and soaked in freshwater for 48+ hours, rinsed with freshwater, then rinsed with distilled-deionized water followed

by two rinses with high performance liquid chromatograph (HPLC) grade water. The carboys were covered with parafilm-covered stoppers for the first water collection and Teflon-covered stoppers for the second collection. For chlorinated hydrocarbon and petroleum hydrocarbon analyses, carboys were washed with Alconox and soaked with freshwater, then rinsed with distilled-deionized water followed by an acid rinse with hydrochloric acid. The carboys were then twice rinsed with HPLC grade water, followed by three rinses with HPLC grade methanol, and finally rinsed three times with Resi-analyzed methylene chloride. After water collection the carboys were capped with Teflon-covered stoppers.

Samples of Hudson-Raritan Estuary water were collected at two different times so as to be able to consider significant differences in water temperature at the time of collection. Water obtained on November 8, 1983, was 12.7°C, and was collected from the NMFS vessel Kyma in Gravesend Bay about 1 mile south of the Verrazano Narrows Bridge, whereas water obtained on March 22, 1984, was 4.4°C, and was collected on the north side of the channel off Shooters Island at the confluence of the Arthur Kill, Kill van Kull, and Newark Bay. For the November collection, sample containers were wrapped in black plastic bags to prevent contact with light. All sampling for both metal and hydrocarbon analyses included time-zero samples collected in small 1- and 4-l containers, respectively. These small containers were filled interspersed with filling 20-l carboys, as described below. Water samples for chlorinated hydrocarbon analyses were collected from an Avon inflatable raft by completely submerging the carboys 0.5 m below the surface, removing the stopper, letting the carboy fill, and replacing the stopper while still submerged. Containers for metals analyses were filled through polyethylene piping using a magnetic drive polypropylene pump with a ceramic spindle. There was no metal contact with the water samples, which were collected 0.5 m below the surface and 2 m away from the boat.

After collection, sample containers were submerged to just below the bottleneck in ambient seawater to which ice had been added. After loading into a truck for transport, all containers were packed in ice. Upon arrival at the Narragansett Laboratory, all containers were transferred into a cold storage room at 2-4°C. Time from collection to cold-room storage was approximately 10 hours. On November 9, samples for the Battelle New England Marine Research Laboratory were packed in ice and transported to Duxbury, Massachusetts.

For the March collection, carboys for all analyses, including those for Battelle, were filled using the same pump and methods as described above. Because of increased biological activity in the warmer months, it was decided that filtered water samples should also be analyzed. To assess the effect of filtering, both filtered and unfiltered water samples were collected and analyzed, with the unfiltered samples collected

first. Filtered samples were collected using an inline "seasoned" cartridge filter with a 3-micron polyethylene filter. Storage and transport of the water to the laboratory used the same protocol as above. Carboys for the Battelle Laboratory were transported on ice to Duxbury, MA, on March 23. Aside from the small, initial (t=o) samples collected on board the R/V Kyma, all other subsampling commenced on March 23.

3. METHODS AND RESULTS OF SPECIFIC STUDIES

3.1 Chlorinated Hydrocarbons

A. G. Requejo, J. Brown, and S. Duffy, Battelle New England Marine Research Laboratory, Duxbury, Massachusetts

3.1.1 Analytical Methods

Samples collected in November consisted of three carboy containers filled with "intact" seawater (i.e. unfiltered with no preservatives or biological inhibitors added). Samples collected in March consisted of four carboy containers, two containing "intact" seawater and two containing seawater which had been filtered to remove particulate matter during collection using an in-line filtration apparatus. In addition to these samples, a partially-filled 20-l container, which had been previously stored since collection at the Narragansett Laboratory, was delivered to Battelle and analyzed along with the fall samples to assess the magnitude of variations in chlorinated hydrocarbon concentrations between individual seawater samples designated for different chemical and biological analyses.

Upon delivery of samples to Battelle, the carboy containers were immediately transferred to a cold (4°C) room. Each container was placed on a stir plate, a Teflon stir bar was added, and the water gently stirred. The outside of each container was covered with a black plastic bag to block out light and the tops were lightly stoppered with a Teflon-coated plug, to permit air exchange.

Subsamples were collected by siphoning 4 liters of seawater into solvent-rinsed amber bottles containing 50 ml of 6N HCl (prepared by dilution with organic-free deionized water) using a U-shaped glass rod. Care was taken to assure that the water came in contact only with Teflon or glass during subsampling. The November samples were subsampled on days 1, 5, 12, and 20 following collection. On days 1 and 5 all three containers were subsampled. One of the three subsamples (replicate 3) was centrifuged in Teflon jars at 2,000 rpm for 20 minutes to remove particulates, and the particle-free seawater extracted and analyzed. The concentrations determined for these centrifuged samples were designated the dissolved concentration, and were subtracted from the average concentration of the other two replicates (replicates 1 and 2, total concentration) to yield an indirect estimate of the particulate concentration. Preliminary

evaluation of these results indicated minimal differences in the concentrations of centrifuged and intact samples, consistent with the observation that the particle content of the seawater was low. As a result, only replicates 1 and 2 were subsampled and analyzed (with no centrifugation) on days 12 and 20. After the final subsampling, the remaining seawater in the carboy containing replicate 2 was discarded and the interior was rinsed with deionized water. The empty bottle was then extracted with hexane, to assess the extent to which adsorption of chlorinated hydrocarbons from the seawater onto the walls of the container was occurring.

The March samples were subsampled on days 1, 5, and 12 following collection. Subsamples collected from each pair of filtered and unfiltered containers were designated as duplicates (i.e. replicate 1 and replicate 2) in order to calculate an average concentration. Since one pair of the winter samples had already been filtered during collection, no centrifugation was employed in their preparation.

Extraction of the acidified seawater was carried out in separatory funnels using hexane (three times, 1:20 solvent:water ratio). The combined extracts were passed through a drying column of Na_2SO_4 concentrated to approximately 5 ul by rotary evaporation, and to 50 ul under a stream of N_2. An internal standard (3,4,5-tribromobiphenyl; TBBP) was added to the combined extracts prior to the concentration step. Preliminary analysis of the concentrated extract by gas chromatography revealed several interfering components of probable biogenic origin: consequently, all extracts were subjected to an additional liquid chromatographic procedure to remove interferences. A Pasteur pipet "column" with a glass wool plug at the base was filled with 1 g of 5% deactivated alumina. After washing the columns sequentially with methylene chloride and hexane, the extracts were added and the columns eluted with 30 ml of hexane to recover the chlorinated hydrocarbons.

The hexane eluant was reconcentrated to 50 ul and analyzed by fused silica capillary gas chromatography employing electron capture detection (GC/ECD) for the following chlorinated compounds: p,p'-DDT, p,p'-DDD, p,p'-DDE, dieldrin, endrin, heptachlor epoxide, chlordane, and polychlorinated biphenyls (as total PCB). Gas chromatography conditions were involved: splitless injection on 30 m x 0.25 mm WCOT SE-52 column temperature from 120 to 290°C/min at 2°C/min. Chlorinated hydrocarbon pesticides in samples were identified by comparison of gas chromatographic retention times with those of individual components in an authentic standard mixture. Concentrations of the chlorinated compounds identified were computed by peak area comparison versus the TBBP internal standard. Quantification of PCBs was conducted by summing the areas of chromatographic peaks matching the retention times of peaks in an authentic mixed PCB standard (consisting of equal amounts of Aroclors 1016, 1242, 1254, and 1260) and comparing the sum to the area of the TBBP

internal standard. An attempt was also made to confirm the presence of the chlorinated compounds identified by GC/ECD by combining several sample extracts to obtain sufficient material to permit analysis by electron impact gas chromatography/mass spectrometry (GC/MS).

To assess the analytical precision and accuracy of the method employed, a standard addition experiment was conducted. A clean, solvent-rinsed carboy container was filled with 20 liters of Duxbury Bay seawater using the laboratory's flowing seawater system. Three 1.8-l subsamples were siphoned into 4-l amber bottles containing 25 ml of 6N HCl, then transferred to 2-l separatory funnels. To each acidified subsample, 20 ng each of authentic Aroclor 1016 and Aroclor 1254 (40 ng total) were added prior to extraction and analysis as described above. The relative standard deviation for the analytically-determined mean PCB concentration calculated from this triplicate standard addition experiment has been designated the analytical precision of the method, and will be used as the interval during which differences in sample concentration over time are not considered significant, i.e. a change in concentration less than the relative standard deviation cannot be distinguished from analytical variability.

Procedural blanks were analyzed with each set of samples by carrying 2 liters of organic-free deionized water through the entire procedure.

3.1.2 Results

Results of the PCB standard addition experiment are shown in Table 1. They are presented both in terms of absolute and percent recoveries and also as added versus calculated concentrations. The high recoveries ($\bar{x}$=22.2 ng/l v. 19.8 ng/l added) indicate that the method employed is capable of excellent quantitative accuracy. The standard deviations shown in Table 1 correspond to an analytical precision of $\pm$ 14%; this value will serve as the criterion by which any changes in chlorinated hydrocarbon concentration over the course of the experiment will be adjudged analytically significant.

Analysis of procedural blanks did not indicate the presence of any contaminants within the analytical range. However, in the gas chromatograms of some samples, the presence of phthalate ester contaminants was observed. The identity of these contaminants was confirmed by GC/MS.

Analysis of the November sample extracts revealed the absence of all the chlorinated compounds of interest with the exception of PCBs. This result was confirmed by GC/MS analyses of the combined extracts, which showed no fragments characteristic of chlorinated compounds other than PCB. Our detection limit for these analyses was approximately 0.2 ng/l for each compound.

Table 1. Results of PCB standard addition experiments.

	Aroclor 1016 + 1254 added	Aroclor 1016 + 1254 recovered	Percent recovery	Added concentration	Calculated concentration
	(Total ng)			(ng/l)	
Replicate 1	40	36.6	91.5	22.2	20.3
Replicate 2	40	30.2	75.5	22.2	16.8
Replicate 3	40	40.1	100.3	22.2	22.3
Mean	40	35.6	89.1	22.2	19.8
Standard deviation	-	5.0	12.6	-	2.8

The average concentrations of PCBs in the November samples, and their variation over the three-week storage period are shown in Table 2. On the basis of our analytical precision criteria of ±14%, there appears to be no significant change in the PCB content of the seawater over time, as values over the three weeks vary by only ± 5-8%. The range of average PCB concentrations found (5.5-6.3 ng/l) is comparable to that reported by Young (1982) for seawater collected in Los Angeles and San Diego harbors (1.8-2.1 ng/l) and in Buzzards Bay (0.7-6.5 ng/l; deLappe et al., 1980).

Boehm (1983) reported particulate PCB concentrations in the Hudson-Raritan Estuary between 0.2 and 3.5 ng/l. Our estimate of particulate PCB concentrations reported in Table 2 (2.0 and 2.4 ng/l for Days 1 and 5, respectively) is within the range of those previously reported and indicates that, in these samples, the estimated contribution of particulate PCB to the total concentration is approximately 33-38%. Thus, the majority of PCBs (62-67%) are either dissolved or water-accomodated.

Duplicate analyses of the additional seawater sample supplied by NMFS-Narragansett with the November samples yielded PCB concentrations of 3.9 and 3.8 ng/l. Analytically, these concentrations are significantly lower than the average values calculated for replicates 1 and 2 (Table 2), although the differences are not great. These results suggest that small differences will occur in the concentrations of PCBs between individual seawater samples.

Table 2. PCB concentrations in Hudson-Raritan Estuary water during a three-week refrigerated storage period (November sampling).

	Concentration (ng/l)				
	Replicate 1	Replicate 2	Replicate 3		
			Average	Particulate*	Dissolved**
Day 1	5.5	6.4	6.0	2.0	4.0
Day 5	6.0	6.5	6.3	2.4	3.9
Day 12	5.5	6.0	5.8	ND	ND
Day 20	4.5	6.5	5.5	ND	ND

ND - Not Determined
* - Average total concentration - dissolved concentration
** - Analytically determined concentration after removal of particles by centrifugation

Analysis of the carboy container "hexane extract" revealed no discernible gas chromatographic PCB pattern, indicating that wall adsorption is not occurring to a significant extent. This result is consistent with the analytically determined concentrations, which are several orders of magnitude below the measured aqueous solubility of PCBs (Griffin and Chian, 1980).

Gas chromatographic analysis of the March samples indicated the presence of two chlorinated hydrocarbon pesticides, p,p'-DDD and p,p'-DDE, in addition to PCBs. Identification of these pesticides was based on coincident gas chromatographic retention times with the respective components in an authentic standard mixture. The low levels present (1-2 ng/l) precluded any confirmation of their identity by GC/MS; our identification must therefore remain tentative. Concentrations of both components were relatively invariant over the two-week course of the storage experiment.

Concentrations of PCBs found in March samples (Table 3) were significantly greater than those found in November samples. This difference does not appear to be due to contamination of March samples by the plastic tubing used during collection, as characteristic contaminants such as the phthalate esters were not detected, and must therefore be attributed to actual compositional differences between seasonal samples (these contaminants might have been removed during the alumina column "clean-up", however). Average PCB concentrations shown in Table 3 for the unfiltered seawater would seem to indicate that its PCB content is increasing with time. This result is actually due in large part to the elevated value obtained for replicate 1 on day 12 (22.8 ng/l v. 15.1-18.7 ng/l for all other values). If this value is disregarded (justified based on a value of 16.2 ng/l for replicate 2, day 12), differences among the remaining values can be accounted solely by analytical variability, indicating that PCB concentrations in fact do not change significantly over the two-week storage period.

The constancy of PCB concentration in unfiltered seawater is supported by the PCB concentrations found in the filtered samples (Table 3), which are slightly more uniform and clearly exhibit no significant change with time. Filtered seawater PCB concentrations over the two-week period vary by only ± 1-7%.

Table 3. PCB concentrations in Hudson-Raritan Estuary water during a two-week refrigerated storage period (March sampling).

	Concentration (ng/l)					
	Unfiltered seawater			Filtered seawater		
	Replicate 1	Replicate 2	Average	Replicate 1	Replicate 2	Average
Day 1	15.1	17.7	16.4	12.5	12.8	12.7
Day 5	16.9	18.7	17.8	14.2	13.2	12.7
Day 12	22.8	16.2	19.5	13.0	14.7	13.9

The differences between average PCB concentrations of filtered and unfiltered water samples represent an indirect estimate of the particulate PCB content of the seawater. This value is 3.7 and 4.1 ng/l for days 1 and 5, respectively, which compares favorably with both the relative contribution of particulate PCBs estimated in November samples using centri- fugation (23% here for both days 1 and 5 v. 33-38% in November samples) and the particulate PCB concentrations measured directly by Boehm (1983). As with the November samples, the majority of PCBs in the March samples (77%) are also associated with the dissolved phase.

3.1.3 Conclusions

The principal conclusions of our laboratory analytical experiment are:

The chlorinated hydrocarbon pesticides selected for quantification (p,p'-DDT, p,p'-DDE, p,p'-DDD, dieldrin, endrin, heptachlor epoxide and chlordane were either absent (<.2 ng/l) or present in trace quantities (1-2 ng/l). Only p,p'-DDD and p,p'-DDE were tentatively identified in the seawater collected during March 1984.

Polychlorinated biphenyls (PCBs) were detected in all samples analyzed. Average total concentrations in seawater collected during March 1984, were 2-3 times greater than those in seawater collected during November 1983 (16.4-19.5 ng/l v. 5.5-6.3 ng/l, respectively).

In both sets of seasonal samples, the majority of PCBs were found associated with the dissolved phase. Particulate PCBs accounted for only 23 and 33-38% of the total concentration in November and March samples, respectively.

No analytically significant changes in seawater PCB concentration were observed during two- and three-week periods of refrigerated storage.

3.2 Polynuclear Aromatics and Other Petroleum Hydrocarbons

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3.2.1 Analytical Methods

Three samples of both the November and March collections of Hudson-Raritan Estuary water were held in capped, 20-l glass carboys at the Narragansett Laboratory for about 3 weeks at 2-4°C in the dark. Subsamples of water for hydrocarbon analysis were collected in precleaned, 1-gallon, glass solvent bottles and either

poisoned with mercuric chloride or extracted immediately. Particulate material was separated from the dissolved fraction by filtration through combusted glass fiber filters (Gelman AE).

Internal standards (anteiso-eicosane and phenanthrene) were added to each sample. Water was extracted twice with dichloromethane. Particulates were extracted by reflux-saponification with methanolic potassium hydroxide. The extracts were transferred into hexane and split into aliphatic (F_1) and aromatic (F_2) fractions by column chromatography. Each fraction was then separated by glass capillary gas chromatography (.34 mm x 30 m fused silica column bonded with 0.2 um film of DB5, temperature programming from 80 to 260°C at 6°/min, flame ionization detector) and quantified using the internal standards.

The precision of this procedure is ± 25% of the mean as determined by replicate samples and intercalibration studies. Details of these studies, as well as a more thorough description of the methods, can be found in Gearing et al. (1978) and Gearing and Gearing (1982).

The two carboy samples from the March collection were also examined microscopically. Particulates were combusted to CO_2 and the stable carbon isotope ratios ($o^{13}C$) determined on a Micromass 602 mass spectrometer. Methods used for these analyses are given in Gearing et al. (1984).

3.2.2 Results

The levels of total hydrocarbons averaged 32 ug/l in November samples (unfiltered), and 42 ug/l in filtered water collected in March. Similar values (36-44 ug/l in Raritan Bay and 24-73 ug/l in the Arthur Kill) were reported by Searl et al. (1977). These levels are typical of urban estuaries (Olsen et al., 1982).

When microscopically examined, the water from the March collection (both filtered and unfiltered) contained predominately amorphous detrital materials. A few larger diatoms (both centric and pennate) also were present. The stable isotope ratio of the whole water was -23.0 o/oo and was increased to -21.9 o/oo by filtration (Table 4). This implies that the larger particulate carbon is primarily terrestrial in origin.

The chemical composition of the hydrocarbons also points to terrestrial and anthropogenic sources. The hydrocarbons consist of 55 to 65% saturates and 35 to 45% aromatics. The saturates contain a large proportion of high molecular weight compounds (indicative of terrestrial material or oil), an equal mixture of n-alkanes with even and odd numbers of carbon atoms (implying a petroleum source), and a high proportion of unresolved compounds (typical of anthropogenic hydrocarbons). The aromatics are predominately larger, less soluble compounds (> 3 rings).

Table 4. Summary of data on water samples.

Type of Data	Date Collected		
	November 8, 1983 (unfiltered)	March 22, 1984 (unfiltered)	March 22, 1984 (filtered)
Total hydrocarbons, ug/l Mean ± 1 std. dev. (number of analyses)	32 ± 4.7 (n=7)	84 ± 14 (n=6)	4.2 ± 5.4 (n=7)
Temporal change (over 3 weeks)	<4 ug/l	<4 ug/l	<4 ug/l
Chemical Distribution:			
% saturates	54	63	64
% aromatics	46	37	36
Physical Distribution:			
% on particles	50	60-70	60-70
Particulate carbon in water, mg C/l	—	1.4	0.93
$o^{13}C$ (particulate matter), o/oo versus PDB	—	-23.0	-21.9

Physically, 50 to 70% of the hydrocarbons were associated with particulate material (> 0.3 um). Within the analytical variability of the method, no differences between the dissolved and particulate-phase hydrocarbons could be proven.

No change with time was found in total hydrocarbons, total F_1 hydrocarbons, or total F_2 hydrocarbons for any of the three samples collected in November (Tables 5-7). There was a change in the ratio of pristane to heptadecane over time in the two water samples from March (Fig. 1). This indicates some biodegradation over time, but affected only a small proportion of the total hydrocarbons present.

3.2.3 Summary

Three samples of Hudson-Raritan Estuary water were collected, held in glass carboys at the Narragansett Laboratory and analyzed for petroleum hydrocarbons over time. Levels of total high molecular weight hydrocarbons ranged from 32 ug/l in the November sample to 84 ug/l in the March sample. Polynuclear aromatics made up 36 to 45% of the total hydrocarbons measured. Up to 70% of the hydrocarbons were associated with particulate material. Concentrations of total hydrocarbons did not change during three weeks of storage.

Table 5. Behavior of hydrocarbons (ug/l) over time - November collection.

Day of experiment	Saturates (F_1)	Aromatics (F_2)	Total hydrocarbons
0	15.9*	15.7*	31.6*
2	14.1	14.8	29.0
4	11.7	14.8	26.5
10	21.4	18.4	39.8
15	18.1	16.3	34.4
20	21.8	8.1	29.9
Average	17.2	14.7	31.9
Standard deviation	4.0	3.5	4.7
Linear regression:			
Slope	0.39	-0.22	0.16
Intercept	13.9	16.6	30.5
Correlation	.76	.51	.27

* Average of duplicate samples

Table 6. Behavior of hydrocarbons (ug/l) over time - March collection (unfiltered).

Day of experiment	Saturates (F_1)	Aromatics (F_2)	Total hydrocarbons
1	54*	40*	94*
5	49	39	88
8	42	18	60
15	55	(31)	(86)
22	63	28	91
Average	53	31	84
Standard deviation	7.8	10	14
Linear regression:			
Slope	0.59	-0.52	0.08
Intercept	47	36	83
Correlation	0.63	0.46	0.04

* Average of duplicate samples

Table 7. Behavior of hydrocarbons (ug/g) over time - March collection (unfiltered).

Day of experiment	Saturates (F_1)	Aromatics (F_2)	Total hydrocarbon
1	28*	12*	40*
5	24	12	36
8	26*	18*	44*
15	30	20	50
22	26	13	39
Average	27	15	42
Standard deviation	2.3	3.7	5.4
Linear regression:			
Slope	0.04	0.13	0.17
Intercept	26	14	40
Correlation	0.15	0.30	0.27

* Average of duplicate samples

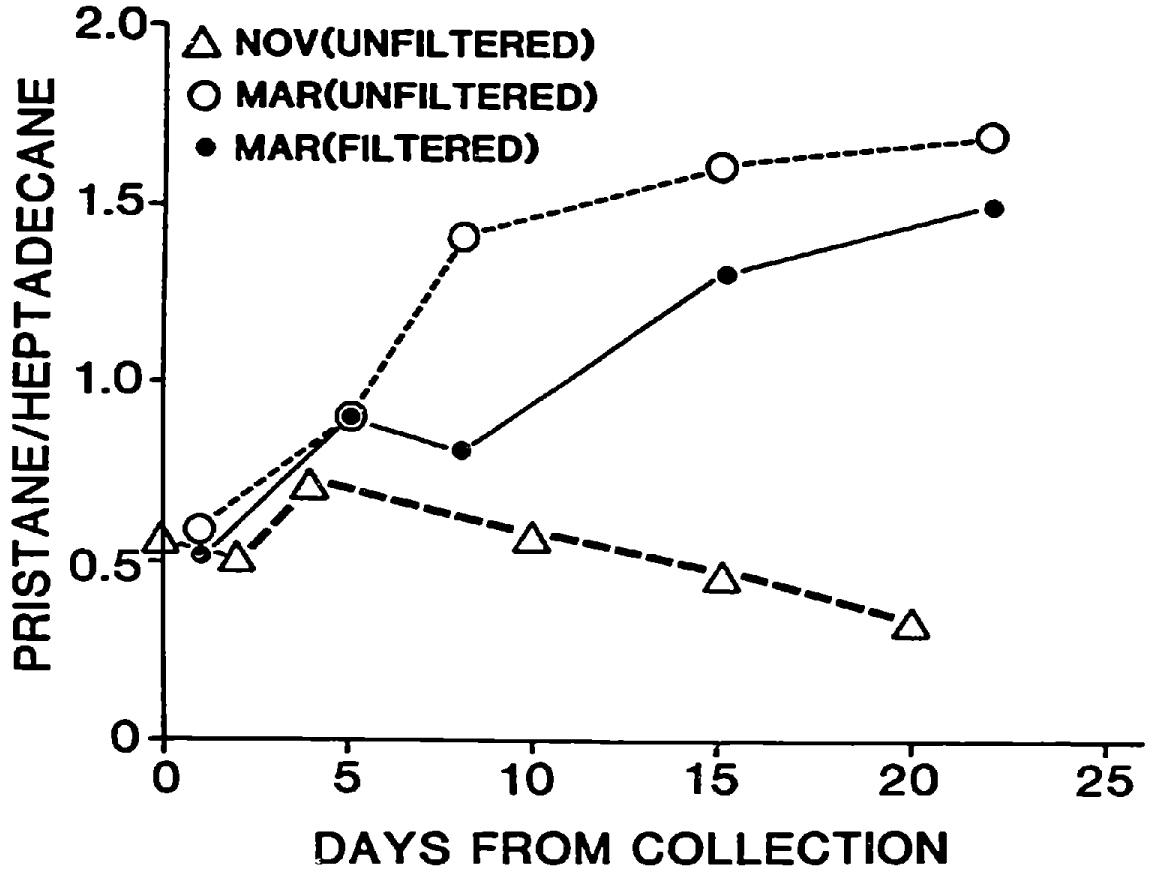

Figure 1. Evidence of biodegradation in water over time.

3.3 Trace Metals

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3.3.1 Analytical Methods

Three carboys from the November 1983 Hudson-Raritan Estuary water collection and two carboys from the March 1984 collection were held as capped, 20-l glass carboys at the Narragansett Laboratory for about 3 weeks at 2-4°C. Along with the carboy collections, three 250-ml, acid-stripped polyethylene bottles were filled with water from the same collection sites to provide the initial trace metal values at the site.

3.3.2 Storage and Sampling

For both the November 1983 and March 1984 water collections, all carboys were placed in refrigerated storage (4°C) for the duration of each experiment (24 days) upon return to the Narragansett Laboratory.

For the November 1983 sampling, water from one of the three carboys designated for trace metal analysis, was filtered through a 0.4 um Nucleopore membrane, and the filtrate transferred to another pre-cleaned glass carboy. The carboy containing the 0.4 um filtered Hudson-Raritan Estuary water was designated as the control, as this stored water permitted examination of the dissolved metal component over the duration of the experiment.

The control carboy and the two remaining unfiltered carboys (carboys #1 and #2) were subsampled at selected intervals over a 23-day period. Sampling began on November 9, 1983 (day 0), the day after water was collected from the Hudson-Raritan Estuary. Subsamples of 250 ml each were taken from each carboy on each sampling occasion. Control subsamples were acidified to pH2, with 6N HCl (G. Frederick Smith, Ultra Pure). Portions of subsamples taken from carboys #1 and #2 were filtered through 0.4 um Nucleopore membranes, and the filtrate acidified to pH2. Unfiltered portions of water taken from carboys #1 and #2 were acidified (pH2), and these samples represent total metal concentrations. Particulate concentrations reported are the result of subtracting dissolved metal from total metal (i.e. unfiltered - filtered = particulate metal).

From the March 1984 collection, subsamples of 250 ml each were taken from both glass carboys at 0, 6, 12, and 24 days. Sampling of the stored water began on March 23, 1984 (day 0), the day after water was collected from the Hudson-Raritan Estuary. Since the stored seawater in this experiment was filtered on the day of collection (3 um), only the dissolved metal component was examined over the course of this storage experiment. In this regard, subsamples were filtered through 0.4 um Nucleopore

membranes and the filtrate acidified to pH2. Analysis of dissolved metal in this experiment permitted direct comparison with dissolved metal of the earlier storage experiment.

All water samples were analyzed by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer Model 5000 AAS equipped with a Perkin-Elmer 500 Heated Graphite Furnace and Zeeman background correction. Sample and standard absorbances were measured by the direct injection of acidified seawater into the heated graphite furnace. It should be noted that the salinity of seawater standards was closely matched to that of the samples, as salinity can affect the absorbance of some metals. Sample concentrations were calculated by comparing averaged sample absorbances to absorbances of known trace metal levels in a similar seawater-HCl matrix.

In the November experiment, dissolved and particulate cadmium, manganese, copper, nickel, and iron were measured in the initial water samples of the Hudson-Raritan Estuary and monitored during the carboy storage experiment.

In the March experiment, dissolved cadmium, manganese, copper, nickel, and lead were analyzed in initial Hudson-Raritan Estuary water samples as well as in the stored water. Iron was not analyzed in this experiment because of problems arising from sampling in a contaminated environment (NMFS cold locker). An attempt was made to determine the lead concentrations in samples of the March experiment, but all samples analyzed were below the detection limit of the direct injection method; the detection limit for lead is on the order of 0.8 ug/kg.

3.3.3 Results

For both the November 1983 and March 1984 initial water collections, the dissolved and/or particulate metal levels observed for each metal at each Hudson-Raritan Estuary collection site fall within the metal ranges observed for other estuarine environments. In all cases, initial metal concentrations of the November 1983 collections (Table 8) were less than those of the March 1984 collections (Table 9).

Within analytical uncertainty, the introduction of Hudson-Raritan Estuary water to glass storage vessels did not immediately alter any of the trace elements that were analyzed (compare Table 8 metal levels with day 0 values of Table 10). This indicates that the glass carboys were clean with respect to trace metals at the time of water collection, and that alterations in trace metal levels during glass storage could be attributed to metal interactions with the storage vessel or to dissolved-particulate interactions.

Table 8. Dissolved and particulate metal concentrations in water taken from the Hudson-Raritan Estuary on November 8, 1983. Individual metal concentrations along with the mean and standard deviation (SD) are reported for each metal.

	Dissolved Metal (ug/kg)									
	Cd		Mn		Cu		Ni		Fe	
	Diss.	Part	Diss.	Part	Diss.	Part.	Diss.	Part.	Diss.	Part.
Boat #1	0.20	-	26.7	2.8	1.08	0.33	3.06	und	2.2	60.7
Boat #2	0.14	-	23.8	4.3	1.07	0.31	2.95	"	2.2	62.2
Boat #3	0.17	-	23.6	3.1	1.07	0.49	2.93	"	1.9	70.2
Dissolved metal										
Mean ± SD	0.17 ± .03		24.7 ± 1.7		1.07 ± .01		2.98 ± .07		2.1 ± 0.2	
Particulate metal										
Mean ± SD		-		3.4 ± 0.8		0.37 ± 0.1		und		64.4 ± 5.1

Table 9. Dissolved metal concentrations in water from from the Hudson-Raritan Estuary on March 22, 1984. Individual metal concentrations along with mean concentrations are reported for each metal.

	Dissolved metal (ug/kg)				
	Cd	Mn	Cu	Ni	Pb
Boat #1	0.25	57	1.6	5.0	ND*
Boat #2	0.28	56	2.2	5.4	ND
Dissolved metal Mean	0.27	57	1.9	5.2	ND

* ND - Not Detectable

3.3.3.1 Cadmium

For the November experiment, dissolved Cd concentrations increased in the control by about 24% during the 23-day storage experiment, indicating that glass-carboy storage enhanced dissolved Cd concentrations (Table 10). The analytical precision for Cd is on the order of ± 5%, thus the values of dissolved Cd at the end of the storage experiment represent a significant increase over initial values.

Total cadmium concentrations were measured in Carboys #1 and #2 in this particular experiment as the dissolved metal samples were contaminated during sample transfer or manipulation. For both carboys #1 and #2, total Cd concentrations increased during the course of the storage experiment with final concentrations about 37% higher than initial levels (Table 10, Fig. 2). The increase in Cd levels in each carboy over the course of the experimental period indicates that Cd is being introduced to the stored seawater. Leaching of Cd from the glass container walls to the stored seawater might explain the increases observed.

For the March samples, dissolved cadmium concentrations at the end of the storage experiment were significantly greater than initial seawater values (Tables 9 and 11, Fig. 3). Cadmium levels in Carboys #1 and #2 were greater than initial levels by 0.09 and 0.17 ug/kg, respectively. Enhanced Cd concentrations in the stored seawater suggest that Cd is leaching from the glass storage vessel, consistent with the November data.

Table 10. Storage Experiment I (November 1983): Summary of dissolved and particulate metal concentrations of the control and experimental carboys over the 23-day duration of the experiment.

	Control	Carboy #1		Carboy #2	
Time	Diss.	Diss.	Part.	Diss.	Part.
			Cadmium (ug/kg)		
Day 0	0.33	0.16		0.18	
Day 1	0.43	0.31		0.33	
Day 3		0.18			
Day 6		0.20			
Day 12	0.34	0.22		0.20	
Day 23	0.41	0.22		0.25	
			Manganese (ug/kg)		
Day 0	24.2	22.3	5.1	23.7	4.2
Day 1	24.1	21.9	5.6	23.4	3.7
Day 3		21.4	5.2		
Day 6		20.2	7.0		
Day 12	23.4	18.9	9.0	21.6	4.1
Day 23	23.7	16.6	1.0	19.0	8.2
			Copper (ug/kg)		
Day 0	1.8	1.2	0.4	1.2	0.4
Day 1	1.8	1.4	0.3	1.3	0.6
Day 3		1.4	0.4		
Day 6		1.6	0.5		
Day 12	2.1	1.8	und	1.6	0.3
Day 23	2.1	1.7	und	1.4	0.3

Table 10. (continued).

	Control	Carboy #1		Carboy #2	
Time	Diss.	Diss.	Part.	Diss.	Part.
			Nickel (ug/kg)		
Day 0	3.0	3.4	und	3.1	0.1
Day 1	3.0	3.8	"	3.1	und
Day 3		3.5	"	"	
Day 6		3.5	"		"
Day 12	3.1	3.6	"	3.2	"
Day 23	3.0	3.5	"	3.1	"
			Iron (ug/kg)		
Day 0	6.2	1.9	65.	1.9	83.
Day 1	5.2	2.8	42.	2.7	67.
Day 3		9.4	57.		
Day 6		2.1	66.		
Day 12	7.2	2.6	62.	2.4	62.
Day 23	6.5	1.0	1.	0.8	54.

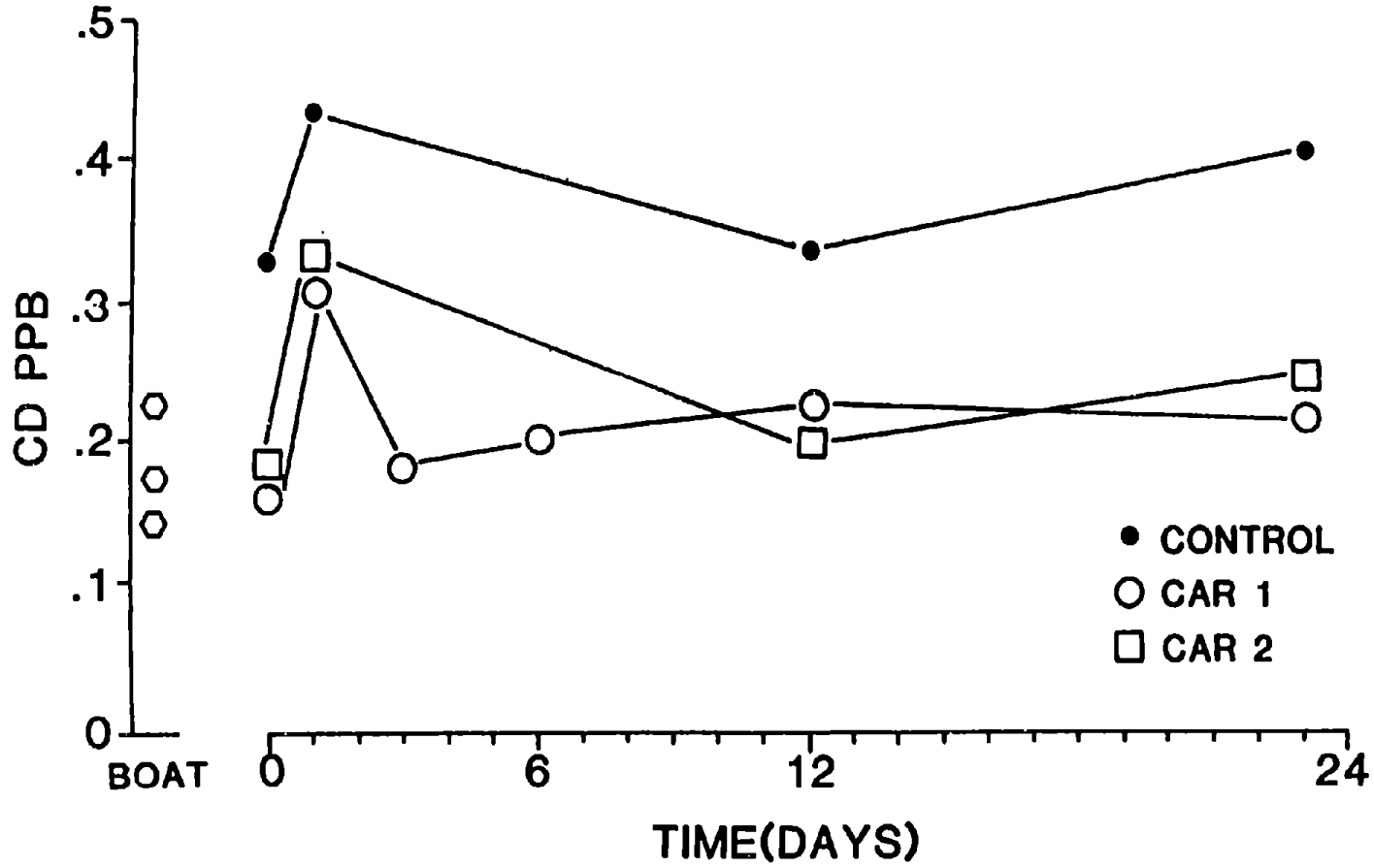

Figure 2. Storage experiment I (November, 1983). Total cadmium concentrations (ug/kg) of initial boat samples and carboy storage samples.

Table 11. Storage Experiment II (March 1984): Summary of dissolved metal concentrations of experimental carboys over the 24-day duration of the experiment.

Time	Carboy #1	Carboy #2	Time	Carboy #1	Carboy #2
Dissolved cadmium (ug/kg)			Dissolved manganese (ug/kg)		
Day 0	no data	no data	Day 0	no data	no data
Day 6	0.35	0.29	Day 6	61	58
Day 12	0.28		Day 12	56	59
Day 24	0.36	0.44	Day 24	61	59
Dissolved copper (ug/kg)			Dissolved nickel (ug/kg)		
Day 0	no data	no data	Day 0	no data	no data
Day 6	2.0	2.7	Day 6	5.8	6.1
Day 12		2.3	Day 12	7.6	5.6
Day 24	3.1	2.6	Day 24	15.4	6.0

3.3.3.2 Manganese

Dissolved Mn concentrations in the control carboy for the November samples did not significantly change over the duration of the experiment, indicating that storage in glass did not affect the dissolved concentrations of this metal. The analytical precision for Mn is about ± 5%.

In each of the test carboys dissolved Mn concentrations decreased with a corresponding increase in particulate Mn. Dissolved concentrations dropped by 26 and 20% in carboys #1 and #2, respectively, while particulate Mn concentrations nearly doubled in each carboy over the study period (Table 10, Fig. 4). For Mn, it appears that the particulate matter present in carboys #1 and #2 scavenged the dissolved metal. Within analytical uncertainty there was no change in the total concentration of Mn (dissolved + particulate, Table 10) in either of these carboys, an observation consistent with the control carboy. The only changes occurring in carboys #1 and #2 appeared to be the partitioning of Mn between dissolved and particulate metal.

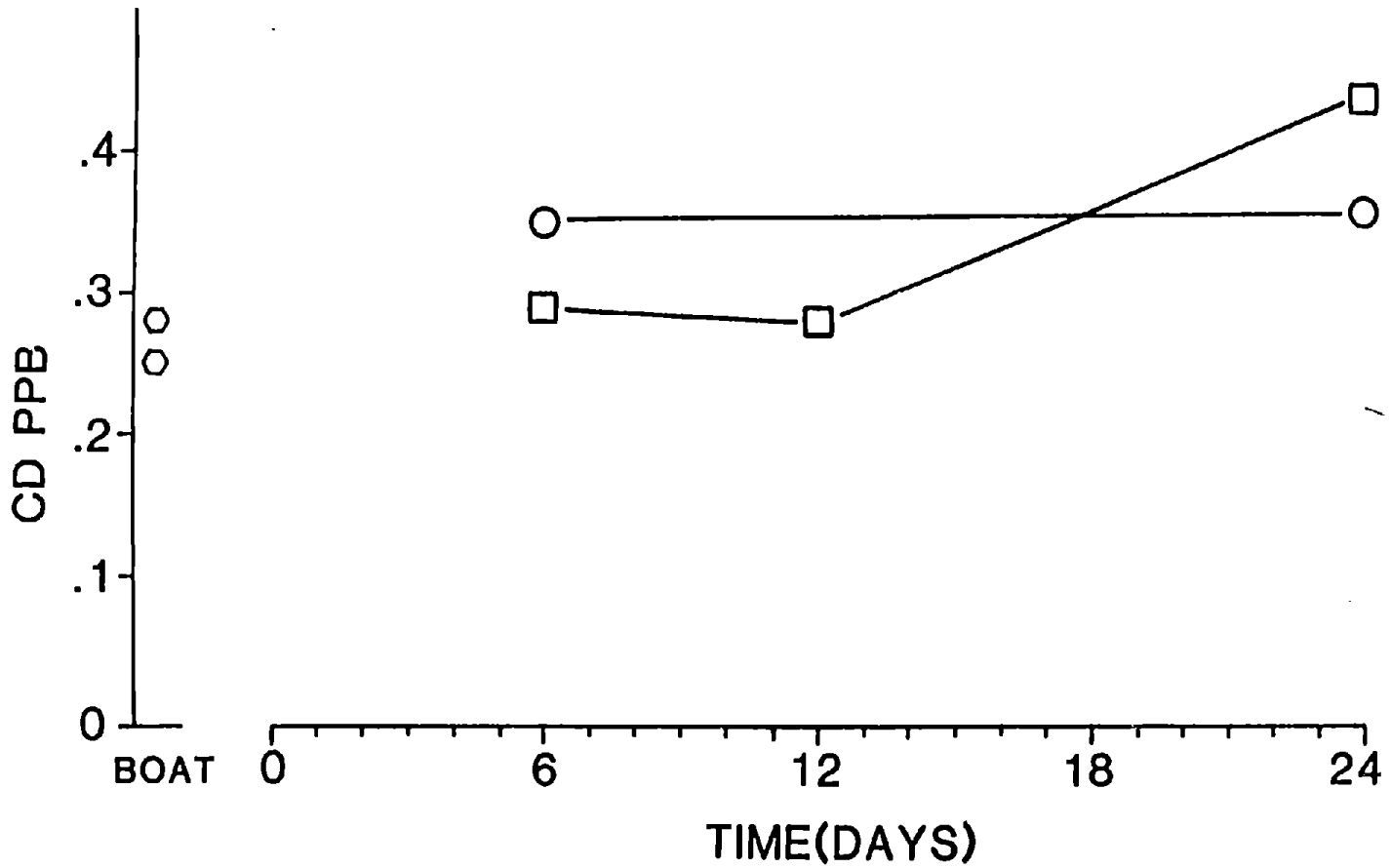

Figure 3. Storage experiment II (March, 1984). Dissolved cadmium concentrations (ug/kg) of initial boat samples and carboy storage samples.

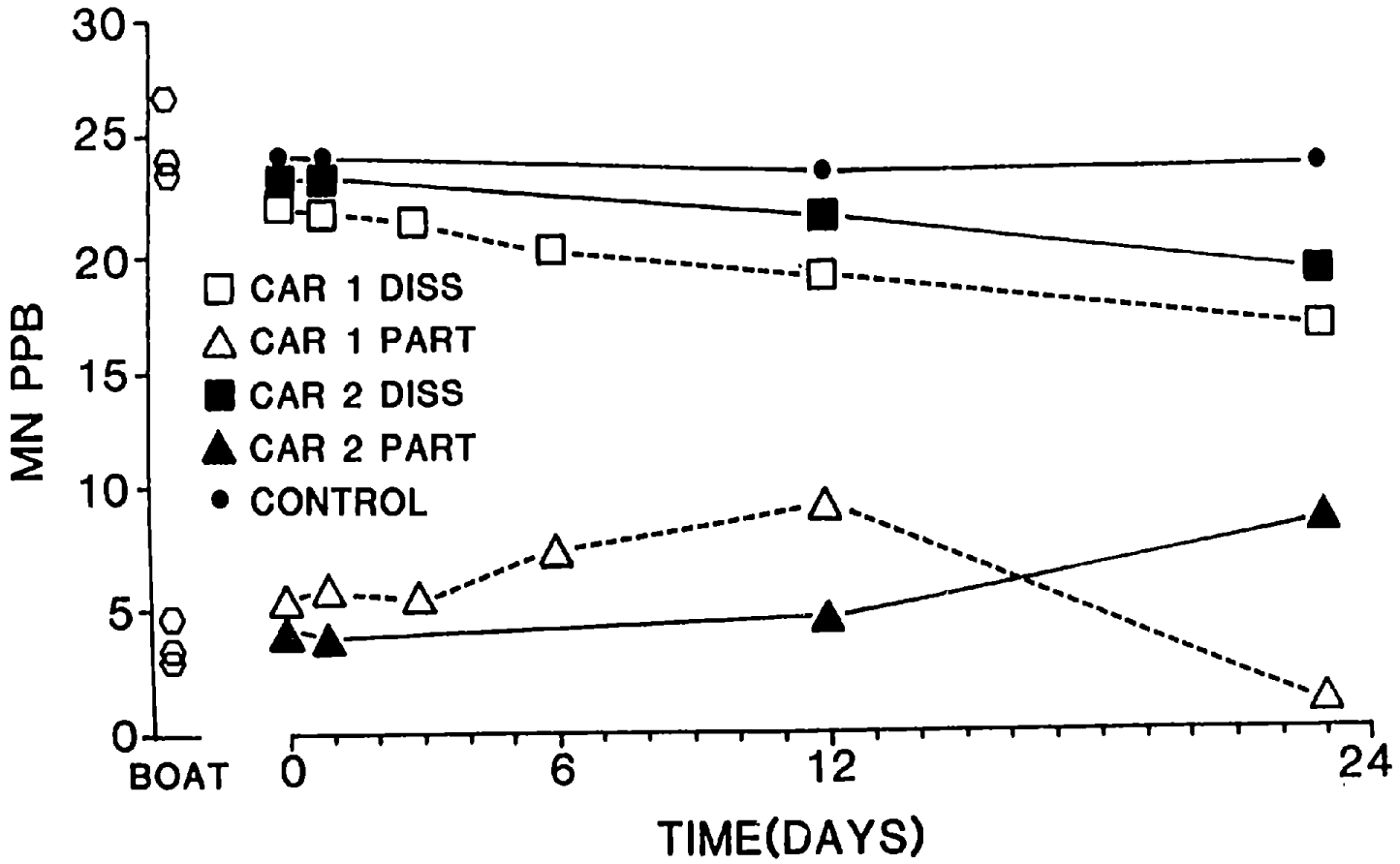

Figure 4. Storage experiment I (November, 1983). Dissolved and particulate (diss. and part.) manganese concentrations (ug/kg) in initial boat samples and in carboy storage samples.

Over the course of the storage experiment for the March sample, dissolved manganese concentrations did not differ significantly from initial seawater values (Tables 9 and 11, Fig. 5). In this case, dissolved Mn levels for both carboys remained at about 60 ug/kg. These results indicate that Mn concentrations are not enhanced by glass storage, an observation consistent with the November storage experiment.

3.3.3.3 Copper

Dissolved Cu concentrations in the control carboy for the November sample increased by 0.3 ug/kg (17%) over initial values during the 23-day experiment. This change was marginally significant as the analytical precision for copper is ± 7%. In this respect it appears that dissolved copper concentrations were only slightly affected by storage in the glass carboys used.

Dissolved Cu levels in test carboy #1 increased from 1.2 to 1.7 ug/kg, an increase of 41%, while particulate Cu fell from 0.4 ug/kg to undetectable levels (Table 10, Fig. 6). In this carboy it is not certain whether increasing dissolved Cu levels at the end of the experiment were due to decreasing particulate concentrations, additions from the storage vessel, or the combined result of metal partitioning and leaching. In carboy #2, final dissolved and particulate copper concentrations were marginally enhanced from initial storage values. In the case of copper, only one carboy in three demonstrated significant concentration changes during the course of the experiment.

After 24 days of storage in glass, dissolved copper levels in carboys #1 and #2 from the March sample were significantly greater than initial seawater concentrations (Tables 9 and 11, Fig. 7). In carboy #1 dissolved Cu concentrations increased from 1.9 to 3.1 ug/kg, an increase of 63%. In carboy #2 final copper levels were 0.7 ug/kg greater than initial levels, an overall increase of 37%. The results of this experiment differ from those of the November experiment in that both of the March experimental carboys demonstrated significant elevations in dissolved copper over the course of glass storage. Only one in three November carboys exhibited significant concentration changes over the experiment's duration. Introduction of copper from the glass walls of the storage vessel to the stored seawater might explain the elevated copper levels observed.

3.3.3.4 Nickel

Dissolved nickel concentrations did not change in the control, from the November sample, which indicates that dissolved Ni was not lost to the walls of the vessel or introduced to the solution by storage. The analytical precision for Ni is about ± 10%.

Within analytical uncertainty dissolved Ni concentrations remained the same throughout the storage experiment (Table 10,

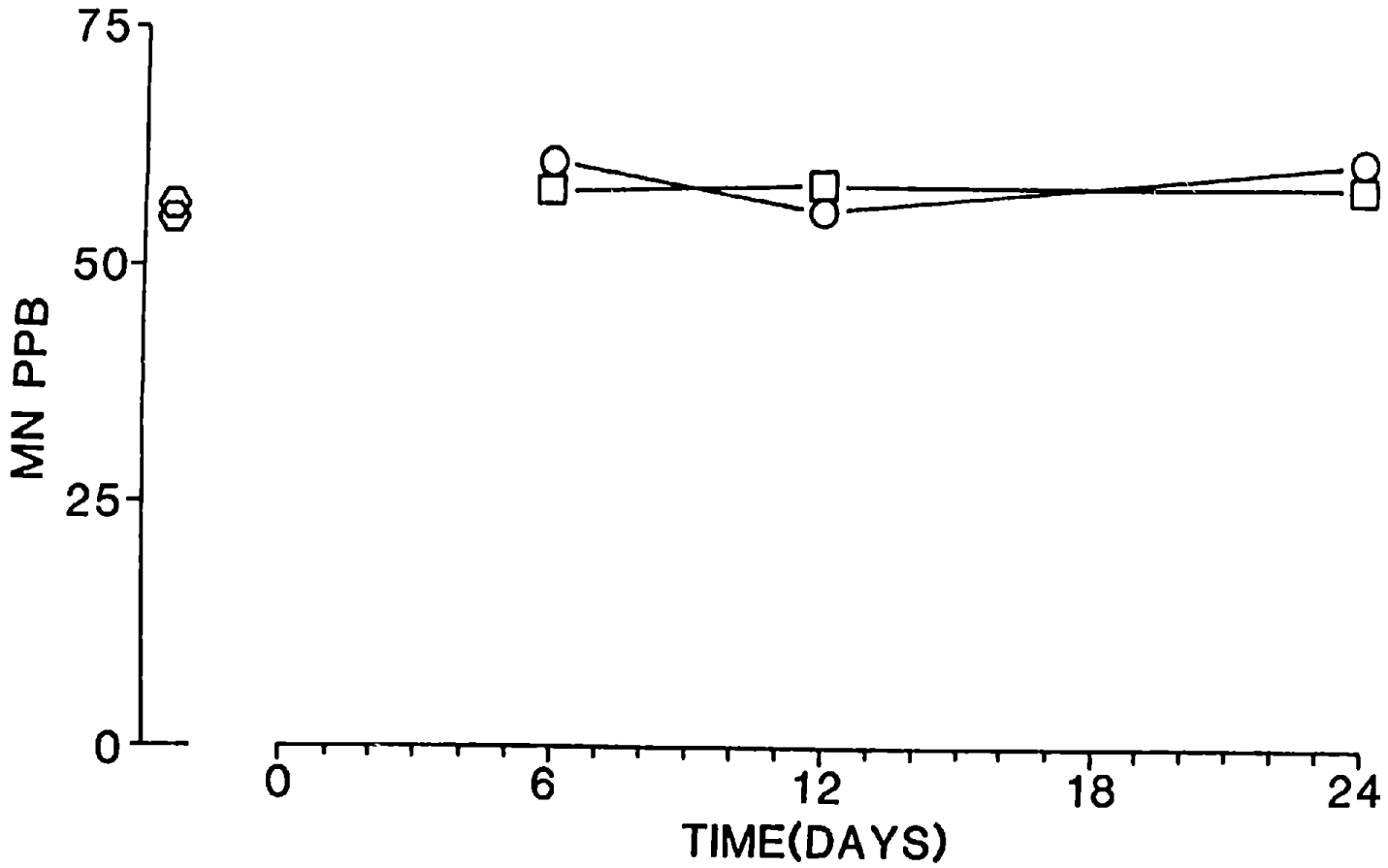

Figure 5. Storage experiment II (March, 1984). Dissolved manganese concentrations (ug/kg) of initial boat samples and carboy storage samples.

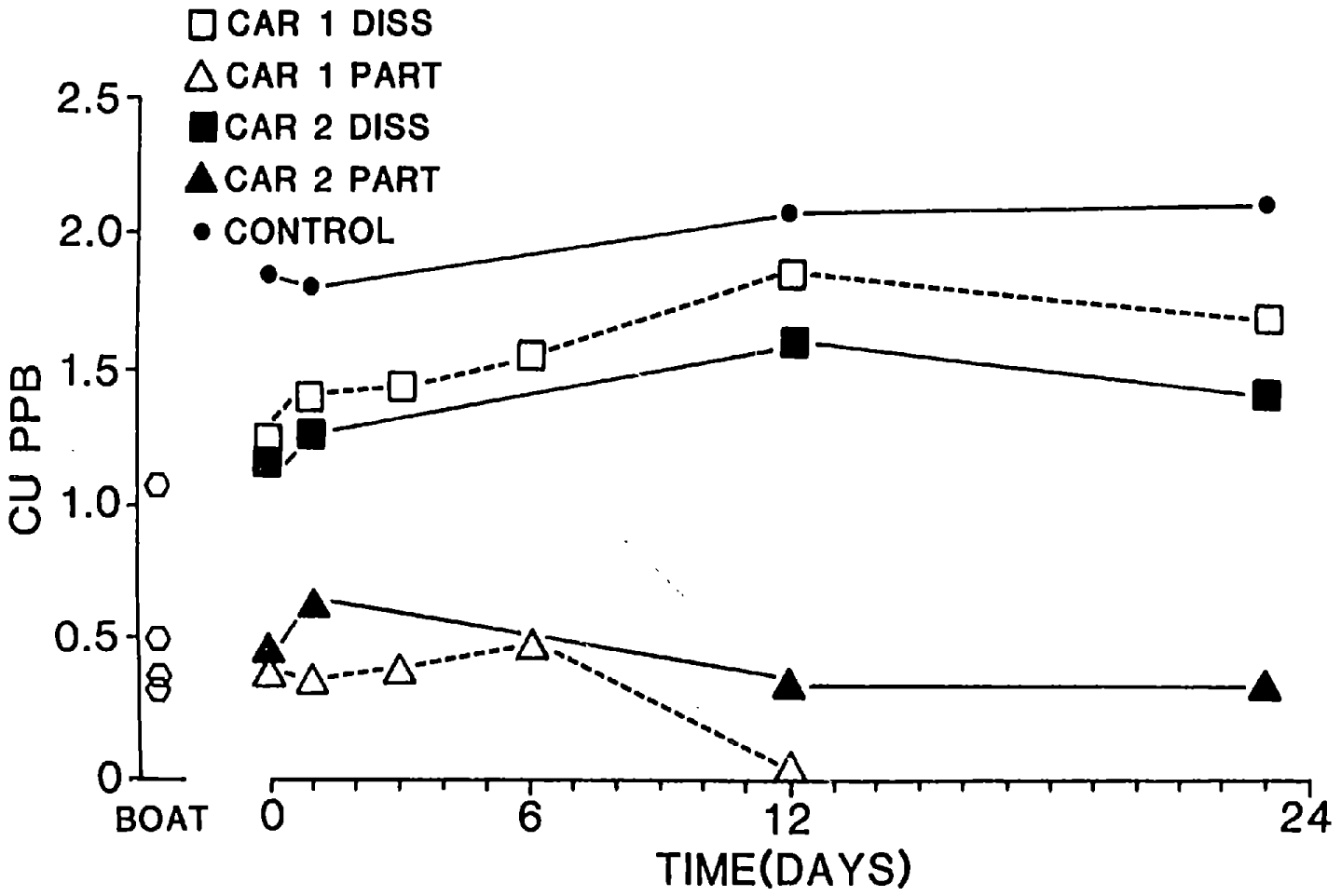

Figure 6. Storage experiment I (November, 1983). Dissolved and particulate (diss. and part.) copper concentrations (ug/kg) in initial boat samples and in carboy storage samples.

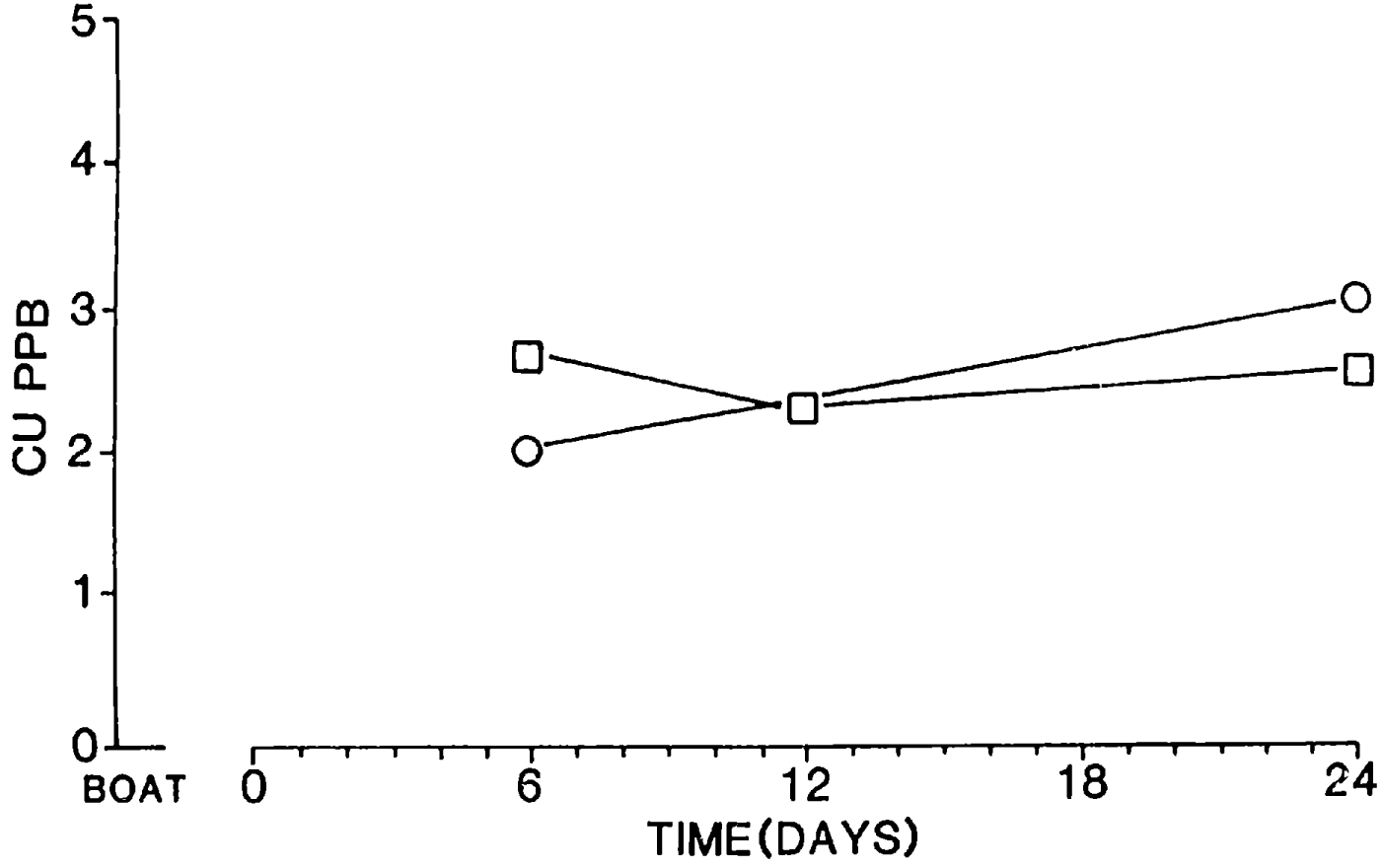

Figure 7. Storage experiment II (March, 1984). Dissolved copper concentrations (ug/kg) of initial boat samples and carboy storage samples.

Fig. 8) in carboys #1 and #2. Particulate Ni concentrations in all but one instance were less than 0.1 ug/kg. These results indicate that Ni is not affected by glass storage over the duration examined.

For the March sample, dissolved nickel concentrations in carboy #1 were three times greater at the end of the storage experiment than initial nickel levels (Tables 9 and 11, Fig. 9). In contrast, carboy #2 demonstrated no significant change from initial dissolved nickel values over the 24-day duration of the experiment (Tables 9 and 11, Fig. 9). The lack of change of dissolved nickel in carboy #2 is consistent with the observations of the November experiment, where nickel concentrations remained the same during the storage period.

3.3.3.5 Iron

Dissolved iron concentrations in the control sample from the November collection were elevated in this carboy relative to the other carboys and the initial Hudson-Raritan Estuary water samples (Tables 8 and 10). The elevated concentrations observed might be attributed to the initial filtration of this sample in the less than ideal environment of the NMFS cold locker. Despite the contamination present, it does not appear that the glass carboy significantly enhanced dissolved Fe during storage (Table 10, Fig. 10). The analytical precision of Fe is on the order of $\pm$ 10%.

Because of the variable dissolved and particulate concentrations observed over the storage period, it is difficult to assess whether glass storage had any effect on Fe levels in both test carboys. Iron was not measured in the March sample due to problems arising from sampling in a contaminated environment.

3.3.4 Summary

It was shown that cadmium concentrations of stored seawater increased significantly in all storage experiments, indicating cadmium is added to solution during storage in the glass carboys used.

Manganese was not added to solution from glass storage. In the first experiment (November 1983), dissolved manganese was scavenged by particulate material, though total manganese (dissolved + particulate) remained constant over the storage period. In the March experiment, dissolved manganese remained constant throughout storage.

Copper concentrations were enhanced with storage in glass. In three of the five carboys examined in the two storage experiments, copper concentrations increased significantly during glass storage. Much greater changes in copper concentration were evident in the March 1984 storage experiment relative to the November 1983 experiment.

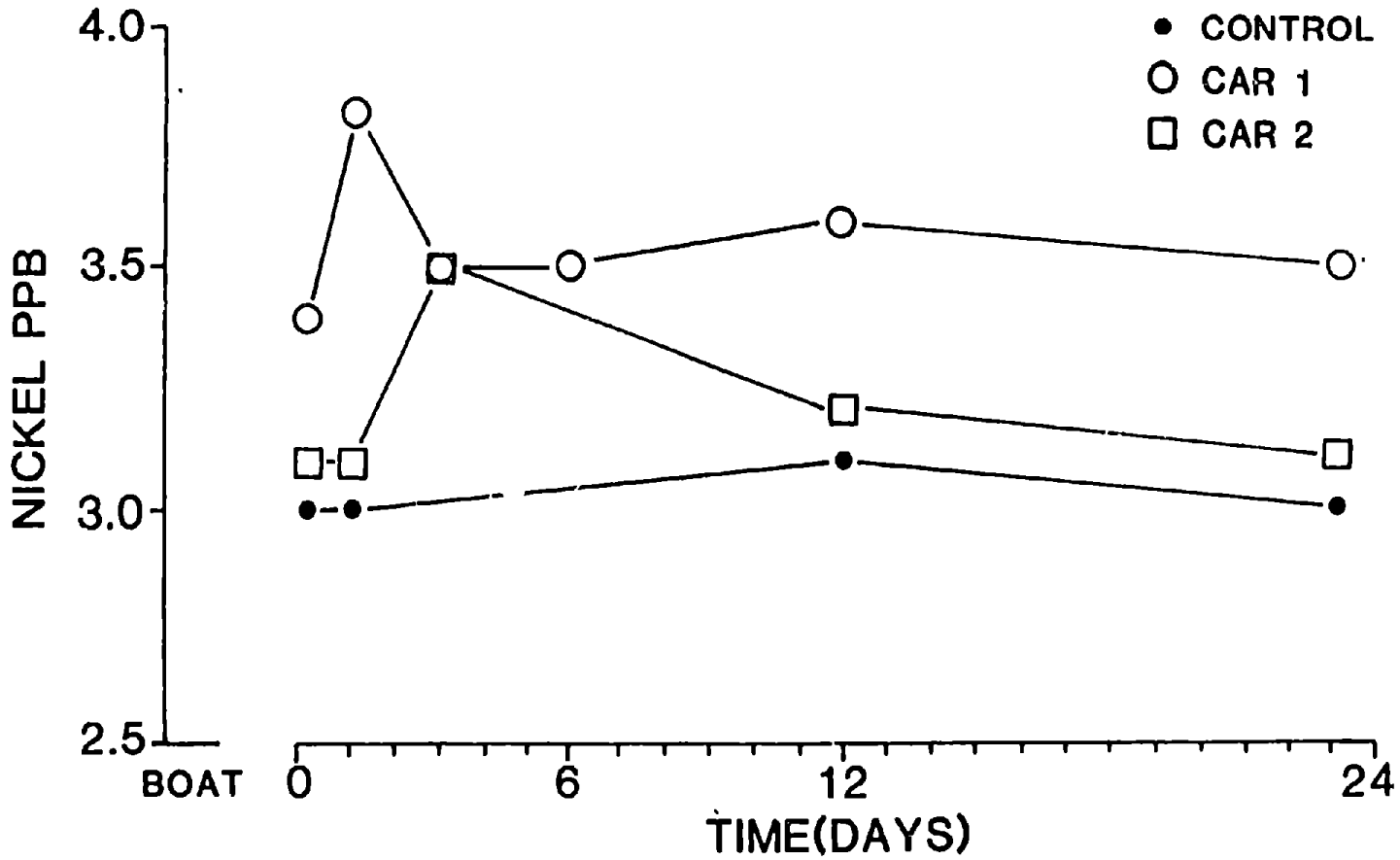

Figure 8. Storage experiment I (November, 1983). Dissolved nickel concentrations (ug/kg) in initial boat samples and in carboy storage samples.

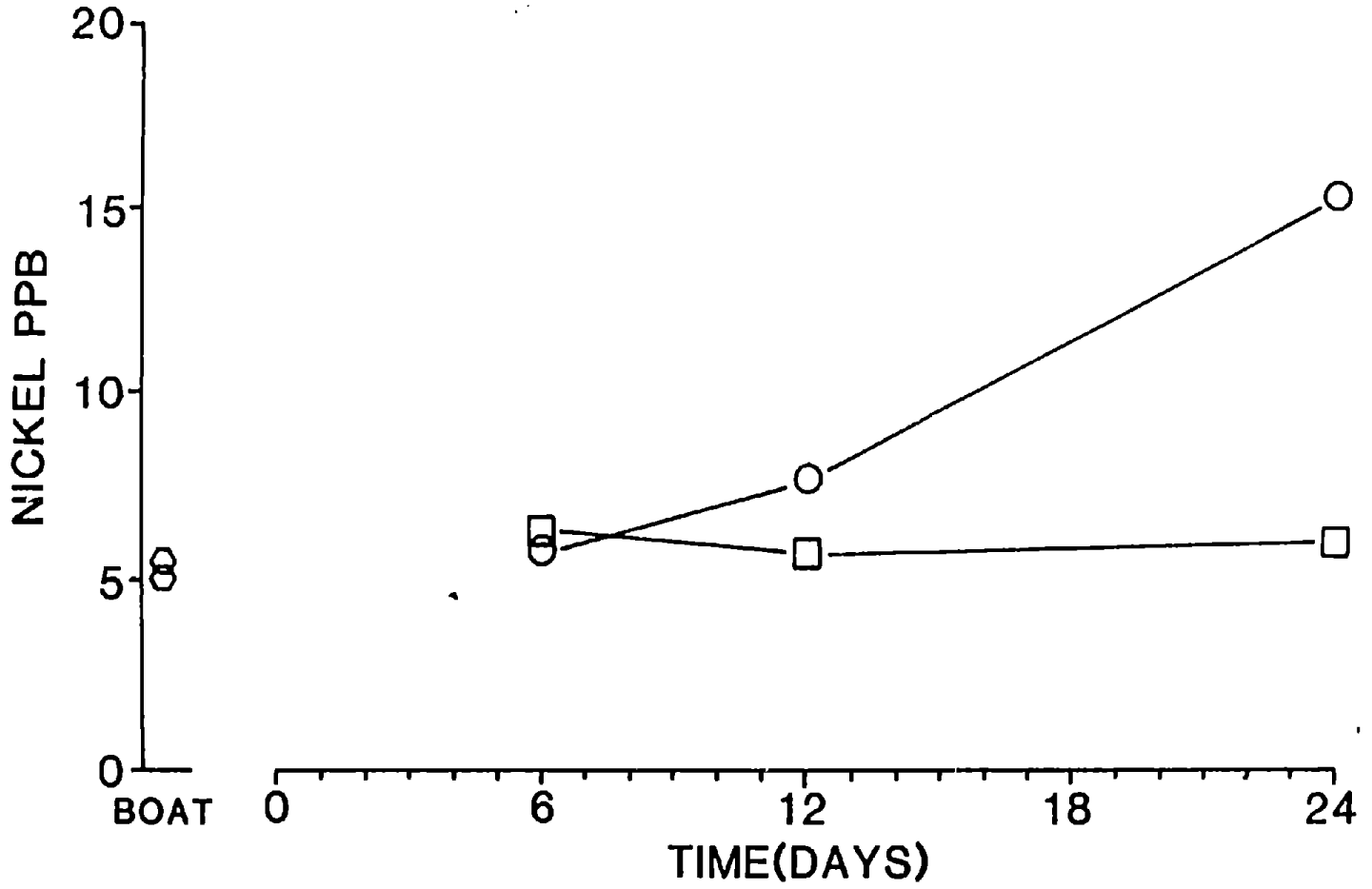

Figure 9. Storage experiment II (March, 1984). Dissolved nickel concentrations (ug/kg) of initial boat samples and carboy storage samples.

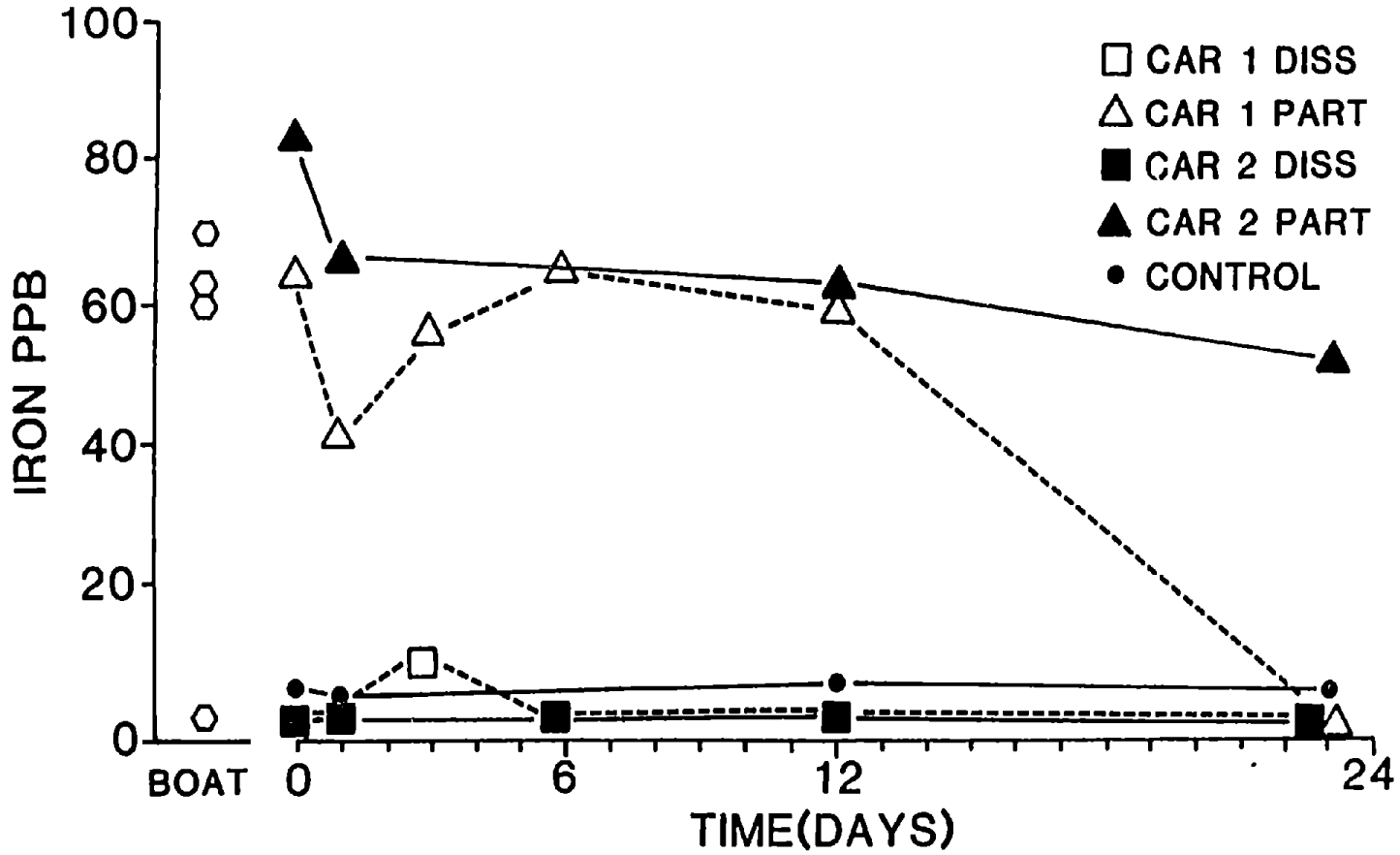

Figure 10. Storage experiment I (November, 1983). Dissolved and particulate (diss. and part.) iron concentrations (ug/kg) in initial boat samples and in carboy storage samples.

Nickel concentrations in four of the five carboys examined in both storage experiments remained at initial nickel levels, indicating that nickel was not lost to the storage walls or introduced to the seawater by glass storage.

Due to the variability encountered and contamination present, it is difficult to determine whether glass storage affected iron levels of stored water.

Lead concentrations were below detection in the March experiment. The detection limit for lead using the direct injection technique is on the order of 0.8 ug/kg.

4. DISCUSSION

There is a growing concern that contaminant levels in certain inland and coastal waters have reached concentrations sufficiently high to affect adversely the more sensitive species. Evaluating the effects of contaminants on the ability of fish and shellfish populations to maintain their numbers within an acceptable range is an important aspect of recruitment studies. The early life history stages, during which the year class strength is determined, have been shown to be the most sensitive to stress, both natural and anthropogenic (Rosenthal and Alderdice, 1976). The focus of future contaminant research, therefore, must be on factors affecting the quality of aquatic habitats and, subsequently, the number and quality of eggs and larvae produced (parental factors) as well as the growth and survival of pre-recruits (eggs, larvae and juveniles).

Basically there are four approaches to experimental exposures of aquatic organisms for the purpose of evaluating contaminant effects: 1) "in situ" studies using cages or open mesh bags, 2) on-site laboratory studies using flow-through systems, 3) remote laboratory studies using a single chemical or mixtures to stimulate environmental exposure, and 4) remote exposure to water collected on site. Of the four approaches, "in situ" (1) or on-site (2) studies are often the most desirable but not always possible due to practical considerations, including physical siting and budget. Exposure studies using a single chemical or mixture of chemicals (3) are useful and have provided the large preponderance of information available on fish and shellfish toxicology, but fall short when the goal is to assess the effects of ambient conditions existing in aquatic environments on the ability of populations to maintain their numbers. Part of the problem arises from an inability to duplicate or assess fully exposure conditions, i.e. synergisms, etc. Problems arise when myriads of contaminants are discharged into the aquatic environment, then mix and subsequently interact with environmental factors such as salinity and dissolved and particulate materials. These interactions can affect chemical speciation and the mode of exposure. The fourth approach can eliminate many of these problems since the bioassays use ambient water, but potentially suffers from other problems associated

with water collection, transportation, and storage. The present study was undertaken to assess the severity of these problems by repeated chemical analysis of refrigerated seawater at different times during storage.

There are numerous reports in the literature describing the changes in contaminant levels following a chemical spill or during the course of a laboratory bioassay. There is also an extensive literature describing changes in "uncontaminated" freshwater and seawater subsequent to collection and storage. Similar changes would be expected to occur during the collection and storage of contaminated" water. Questions that arise are, what is the magnitude of the chemical changes involved and what is their significance to bioassay results?

In this study we did not analyze for all elements or compounds that might be found in the Hudson-Raritan Estuary. A subset of chemicals or chemical classes was selected based on toxicity, i.e. biological effects, expected concentration in the Hudson-Raritan Estuary, and practical analytical considerations. This subset should be indicative of changes that occur during collection and storage. The choice of collection, transportation, and storage procedures, all of which could potentially affect the outcome of this study, was the result of a series of compromises based on often conflicting considerations. For example, plastic containers are the norm for storage of seawater for trace metal analysis and glass is used for organic analysis. We feel that, for the purpose of bioassays, it is best to use whole-water samples without filtration or other treatment to remove particulate material. However, it may be desirable under conditions of high particulate content, such as during the spring phytoplankton bloom, to filter the water prior to storage. The results of this study suggest that this can be accomplished with minimal effect on contaminant levels in the soluble fraction.

It should be remembered that the goal of this study was to assess the effects of existing contaminant levels in the Hudson-Raritan Estuary on the ability of fish and shellfish to maintain acceptable population levels. It was not our goal to assess the impact of a particular chemical spill or discharge. Much of the weathering, volatilization and chemical and biological degradation of specific components would have occurred prior to collection of the water. We see only the more stable components, degradation products or metabolites. These, however, are precisely the components of interest in assessing the impact of the chronic or background level of contamination currently existing in the Hudson-Raritan Estuary. Consequently, it is not surprising that for most of the chemicals and chemical classes examined in this study, no analytically significant changes in concentrations were observed in Hudson-Raritan Estuary waters during refrigerated storage up to 3 weeks. Where analytically significant changes were observed, such as with certain of the trace elements, the magnitude of the observed changes in

concentration did not appear to be sufficiently large to affect bioassay results. Based on these findings, it appears that studies involving bioassays using stored water collected at a site remote from the laboratory are a viable approach to assessing the effects of chronic contaminant levels on resident populations.

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39. **USA Historical Catch Data, 1904-82, for Major Georges Bank Fisheries.** By Anne M. T. Lange and Joan E. Palmer. May 1985. iii + 21 p., 12 figs., 2 tables. NTIS Access. No. PB85-233948/AS.

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