

NBP-88-12A

Mercury in the Waters of

Narragansett Bay 35 pp

Vandal & Fitzgerald (UConn)

Narragansett Bay Estuary Program

Current Report

The Narragansett Bay Project

Mercury in the waters of Narragansett Bay

G.M. Vandal and W.F. Fitzgerald
Department of Marine Sciences and
Marine Sciences Institute
The University of Connecticut
Groton, CT 06340

Report #NBP-88-12A

LOAN COPY
Please return to:
Narragansett Bay Project
291 Promenade St.
Prov., RI 02908-5767



The Narragansett Bay Project is sponsored by
the U.S. Environmental Protection Agency and
the R.I. Department of Environmental Management.



Mercury in the waters of Narragansett Bay

G.M. Vandal and W.F. Fitzgerald
Department of Marine Sciences and
Marine Sciences Institute
The University of Connecticut
Groton, CT 06340

Report #NBP-88-12A

FOREWORD

The United States Congress created the National Estuary Program in 1984, citing its concern for the "health and ecological integrity" of the nation's estuaries and estuarine resources. Narragansett Bay was selected for inclusion in the National Estuary Program in 1984 and designated an "estuary of national significance" in 1988. The Narragansett Bay Project (NBP) was established in 1985. Under the joint sponsorship of the U.S. Environmental Protection Agency and the Rhode Island Department of Environmental Management, the NBP's mandate is to direct a five-year program of research and planning focussed on managing Narragansett Bay and its resources for future generations. The NBP will develop a comprehensive management plan by December, 1990, which will recommend actions to improve and protect the Bay and its natural resources.

The NBP has established the following seven priority issues for Narragansett Bay:

- * management of fisheries
- * nutrients and potential for eutrophication
- * impacts of toxic contaminants
- * health and abundance of living resources
- * health risk to consumers of contaminated seafood
- * land-based impacts on water quality
- * recreational uses

The NBP is taking an ecosystem approach to address these problems and has funded research that will help to improve our understanding of various aspects of these priority problems. The Project is also working to expand and coordinate existing programs among state agencies, governmental institutions, and academic researchers in order to apply research findings to the practical needs of managing the Bay and improving the environmental quality of its watershed.

This report represents the technical results of an investigation performed in support of the Narragansett Bay Project-funded SINBADD cruises (1985-1986). The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement #CX812680 to the Rhode Island Department of Environmental Management. It has been subject to the Agency's and the Narragansett Bay Project's peer and administrative review and has been accepted for publication by the Management Committee of the Narragansett Bay Project. The results and conclusions contained herein are those of the author(s), and do not necessarily represent the views or recommendations of the NBP. Final recommendations for management actions will be based upon the results of this and other investigations.

This report represents a technical contribution to the synthesis report, "Water quality survey of Narragansett Bay: A summary of results from the SINBADD 1985-1986" (report #NBP-89-22). The interested reader is encouraged to investigate this additional source of information.

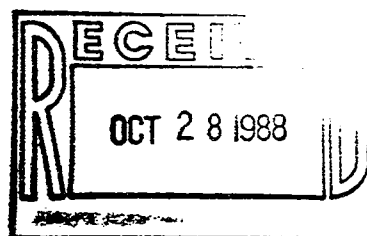
Final Report

Mercury in The Waters of Narragansett Bay

October 19, 1988
for Narragansett Bay Project

by

G.M. Vandal and W.F. Fitzgerald
Department of Marine Sciences and
Marine Sciences Institute
The University of Connecticut
Groton, CT 06340



Mercury in The Waters of Narragansett Bay

by

G. M. Vandal and W. F. Fitzgerald

Abstract

The mercury distribution was determined for the waters of Narragansett Bay and tributaries during a survey conducted April 7 - 10, 1986. "Acid-labile" Hg was determined for filtered (dissolved) and unfiltered (total) samples following acid digestion with ultrapure nitric acid. Total and dissolved acid-labile Hg concentrations were highest in river and point source collections and decreased linearly with respect to increasing salinity suggesting conservative mixing of these fractions. Total acid-labile Hg in unfiltered samples ranged from 35 pM for the flow weighted mean fresh water end member to 5.5 pM in Rhode Island Sound. Dissolved acid-labile Hg for the flow weighted mean fresh water end member and Rhode Island Sound was 22 pM and 2 pM, respectively. The estuarine distribution of acid-labile Hg was similar to other trace metals studied as part of this survey. Cold oxidation with BrCl released additional Hg to unfiltered low salinity samples indicating the presence of a strongly bound form. This strongly bound fraction appeared to be removed with increasing salinity. The flow weighted mean fresh water total Hg concentration was 78 pM following cold oxidation.

1. Introduction

Mercury is transported to coastal waters via rivers and the atmosphere. Mercury enters rivers naturally by way of crustal weathering processes and from anthropogenic sources such as industrial discharges, municipal wastewater effluent, and urban runoff. Mercury is emitted to the atmosphere from natural sources such as soils and plants and human related activities such as sewage treatment, industrial production and the combustion of fossil fuels. A fraction of the Hg released to the atmosphere subsequently enters coastal waters by wet and dry deposition including gas exchange. Mercury in natural waters has the potential to contaminate fisheries due to its tendency to bioaccumulate along tropic levels.

The fate of riverine Hg and its impact on the environment is influenced by physical, chemical, and biological estuarine processes. There is a paucity of reliable data on the factors controlling the behavior of Hg during estuarine mixing. Nonconservative behavior of certain other trace metals during estuarine mixing has been demonstrated. For example, the transformation of dissolved riverine Fe, Mn, Al, Cu, Ni, Co, and Cd to particulate form upon mixing with seawater was confirmed in a laboratory mixing experiment (Sholkovitz, 1978). The postulated mechanism for the observed phase change was flocculation of metals associated with colloidal humic acids and hydrous iron oxides (op.cit.). Model calculations indicate that 90% of the Hg in river water is complexed with humic substances (Mantoura, et al, 1978). Therefore, removal of the dissolved Hg fraction by coflocculation with colloidal humic acids is likely to be

important to the transport of Hg in estuaries. Moreover, nonconservative estuarine behavior of dissolved Hg would depend on the exchange between solid and soluble forms by adsorption/desorption, flocculation of colloids, and potential conversions between the soluble oxidized and insoluble reduced form. Consequently, the estuarine distribution of particulate Hg will be effected by the above processes and, in addition, by the resuspension/deposition of sediment.

1.1 Objectives of Our Study of Mercury in Narragansett Bay

The objectives of our study were as follows: (1) measure total and dissolved Hg in a synoptic survey for Hg in the waters of Narragansett Bay. (2) to assess the role of dissolved and particulate forms in the transport of Hg, (3) to investigate the significance of estuarine removal (i.e. flocculation) or remobilization using the reactant approach.

In the reactant approach the dissolved concentration of the constituent is measured in situ for salinities ranging between fresh water and seawater values. A mixing diagram of concentration versus salinity is generated using salinity as an indicator of mixing. Measured values which coincide with the theoretical dilution line (TDL), a line connecting sea water and fresh water endmember concentrations, suggest conservative behavior. Negative deviation from the TDL indicates removal within the estuary while a positive deviation implies a source. This approach assumes the system to be in a steady state. Information deduced from mixing plots may be inconsistent with estuarine geochemistry if the reactant approach is applied under

non-steady state conditions. For example, unaccounted sources or temporal variability in fluxes may yield a nonlinear estuarine distribution for a conservative constituent .

The synoptic survey was conducted in conjunction with The 1985 Narragansett Bay Project to monitor salinity and chemical contaminants. Thus the estuarine distribution of Hg could be examined with respect to salinity, nutrient concentrations, trace metal, turbidity, suspended solid load, and chlorophyll-a determinations which were measured by other project participants.

2. Experimental Method

2.1. Sampling Locations

In an effort to study a single mixing region in Narragansett Bay, our Hg survey focused on the Western Passage and the Providence River estuary. A map of the sampling locations sampled is given in Figure 1. In order to quantify the flow of Hg into this region, four rivers and four point sources which contribute to the Providence River were sampled. These eight sources to the Providence River are the Blackstone, Woonasquatucket, Moshassuck, and Pawtuxet rivers, Narragansett Bay Commission Fields Point Wastewater Treatment Facility (WTF), East Providence WTF, Blackstone Valley District Commission WTF, and Narragansett Electric Manchester Street cooling discharge. A fresh water endmember concentration was determined by volume weighing these multiple contributions.

The sampling scheme within the estuary emphasized the Providence River and upper Bay stations where the salinity is lowest. Removal of other trace metals by flocculation has been shown to occur at salinities below 15 ppt (Sholkovitz 1976,

1978). Surface collections were obtained at Stations 1 and 2 in the Providence River, Stations 4, 5, 7, 11, 13, in the Western Passage, and Station 22 in Rhode Island Sound. Station 22 was defined as the seawater endmember. Stations 2, 4, and 5 were also sampled at depth in order to assess vertical variability. In addition, a surface collection was obtained from Station 17, at the mouth of the Taunton River.

2.2. Sample Collection and Analysis

For decades marine scientist have attempted to elucidate the processes controlling the transport of Hg from the continents to the oceans. Unfortunately, most Hg measurements made during this time were erroneous due to spurious contamination from improper sampling procedures and inadequate analytical techniques (Fitzgerald, 1979). An intercalibration exercise sponsored by the International Council for the Exploration of the Sea revealed that low level Hg determinations made at many laboratories suffered from systematic errors (Olafsson, 1982). However recently developed ultraclean laboratory techniques and sensitive analytical methods are capable of measuring low levels of Hg in natural waters (Gill & Fitzgerald, 1985, 1987) .

In our study of Hg in Narragansett Bay, two collections were made at each location with rigorously cleaned 2 liter teflon bottles using the careful sampling methods outlined in Gill and Fitzgerald, 1985. River samples were collected by bridge sampling with an acid washed teflon bucket. Paul Desrosiers (Dept. of Environmental Management) collected point source collections by hand directly into a teflon sample bottle. Estuarine stations

were sampled by Carlton Hunt (Univ. of Rhode Island, Graduate School of Oceanography) and co-workers using a teflon pump with the exception of Station 1 which was sampled by hand into the sample bottle. The Hg contribution associated with each sampling technique was assessed with replicate samples taken from the Marine Ecosystems Research Laboratory, Univ. of R.I., header tank. The Hg concentration by the three methods, hand grab, teflon bucket, and teflon pump were not significantly different indicating that none was a source of Hg contamination.

A flow diagram of the experimental procedure is given in Figure 2. A detailed description of sample handling, preparation of reagents, and sample analysis can be found in Gill and Fitzgerald, 1985 and 1987. Sample collections were returned to our class 100 clean laboratory at Marine Sciences Institute, Univ. of Connecticut, Groton, for processing within 3 to 8 hours of collection. Samples were transported in a cooler in order to maintain ambient temperature. One of the replicate collections from each location was filtered through a combusted 0.4 micron glass fiber filter (Gelman Instrument Co.). Combusted glass fiber filters were used because they are free of Hg contamination and can filter 500ml of turbid river water without clogging. The filtrate was collected in an acid washed 2 liter teflon bottle. The duplicate collection was processed unfiltered. A five milliliter aliquot of ultrapure HNO_3 was added per liter of sample. Gold chloride solution was added to river and point source collections to retain Hg in solution in the absence of chloride. The samples were kept sealed on the clean lab bench for 1 month prior to analysis to allow time for

complete acid digestion.

The Hg in the natural water sample which was converted to a readily reducible form by acid digestion or cold oxidation was reduced to elemental Hg with the addition of SnCl₂. The sample was aerated and the Hg trapped on gold coated sand columns. These columns were then transferred to the analytical system, two-stage Au amalgamation with detection by cold vapor atomic absorption spectrophotometry (CVAAS) (Gill and Fitzgerald, 1987). Calibration of the analytical system was carried out on a daily basis by vapor phase addition of Hg saturated air. Aqueous standards prepared from known weight of HgCl₂ were run daily and were generally within 1% of the true value at the 2 ng/L level. The reagent blank from HNO₃ and BrCl was 0.04 ng (0.2pM) and 0.2 ng (1 pM) respectively per liter of sample. The blank associated with the reduction-aeration procedure was 0.07ng/L (0.4pM).

2.2.1. Bromine Monochloride Cold Oxidation

There is evidence in the literature that some forms of Hg present in natural waters are not converted to a readily reducible form with nitric acid treatment. Bromine monochloride (BrCl), which has been shown to be a more effective oxidant of strongly bound forms of Hg (i.e. CH₃Hg⁺) than HNO₃ (Bloom and Crecelius, 1983), was added to the remainder of each unfiltered sample. A detailed description of the cold oxidation procedure is given elsewhere (op.cit.). In brief, 5 ml of the oxidation reagent were added per liter of sample. The samples were shaken vigorously for several minutes and were then allowed to sit for approximately 1 hour. Five milliliters of 12% hydroxylamine

hydrochloride, which reduces BrCl but not Hg^{++} (op. cit.), were added per liter of sample prior to SnCl_2 reduction of aqueous Hg , amalgamation on Au and detection by CVAAS.

2.2.2. Definition of Fractions

Total and dissolved "acid-labile" Hg were determined in unfiltered and filtered samples respectively following 1 month of nitric acid digestion. Particulate "acid-labile" Hg was determined by difference. Total "oxidized" Hg was determined on unfiltered acidified samples which were treated with bromine monochloride. The strongly bound fraction was defined as the difference between the total "oxidized" and total "acid-labile" measurement.

3. Synoptic Survey for Mercury in Waters of Narragansett Bay: Geochemical Implications

The concentrations measured for the various fractions in river and point source collections are given in Tables 1. Results for collections from the Providence River and Narragansett Bay stations are listed on Table 2.

3.1 Mercury in Fresh Water Source to Providence River

The total acid-labile Hg content in the four rivers ranged from 29 pM, in the Woonasquatucket, to 8 pM, in the Moshassuck. The four point sources ranged in concentration from 252 pM, in Fields Point WTF, to 24 pM, in the Narragansett Electric cooling discharge. Concentrations of dissolved acid-labile Hg ranged from 26 pM, in the Woonasquatucket, to 12 pM, in the Blackstone. The point source collections ranged from 68 pM, in Fields Point WTF effluent, to 14 pM, in Narragansett Electric Cooling Discharge.

In Moshassuck River, Pawtuxet River, and Narragansett Electric cooling discharge collections the concentration of total acid-labile Hg was determined to be less than dissolved Hg. Introduction of Hg to the sample during filtration would result in the concentration of Hg being higher in the filtered sample than in the unfiltered collection. However, we found no evidence of contamination when triplicate samples of our cleanest distilled water were passed through the filtration system. These ambiguous results may suggest that dissolved Hg in the unfiltered samples was strongly adsorbed to a solid phase prior to analysis and was not measured by the acid digestion procedure. This hypothesis is supported by the observation that in all samples the total Hg determined using the cold oxidation method was greater than dissolved acid-labile Hg and the Pawtuxet River, Moshassuck River, and Narragansett Electric collections had a very high concentration of strongly bound Hg, see Table 4. Variability in the Hg burden on short time and spatial scales would also explain the observed phenomena because duplicate collections were not obtained simultaneously but were collected in succession within minutes of each other.

Flow data for the rivers and point sources at the time of this survey were obtained through Eva Hoffman (Narragansett Bay Project, DEM). This information was applied in the calculation of flow weighted mean fresh water concentration for this multiple source system. The flow weighted mean was 35 pM for total acid-labile Hg and 22 pM for dissolved acid-labile Hg. This calculation is illustrated in Table 3. In Figures 3, 5, and 6 the TDL was drawn between the calculated fresh water endmember

concentration and the concentration determined for Station 22. The mixing diagrams given in Figures 3, 5, and 6 include data from surface water stations in the Providence River and Western Passage. The TDL in these figures represent conservative mixing of fluvial Hg sources to the Providence River with Rhode Island Sound seawater. Station 17 was excluded from these mixing diagrams because it received additional input from the Taunton River which was not reflected in the flow weighted mean. Deep water Stations 2, 4, and 5 were excluded because they may receive additional input from resuspension of sediments.

3.2 The Estuarine Distribution of Mercury

Fluvial inputs constitute a major portion of the Hg flux to Narragansett Bay. The primary process influencing the distribution of dissolved acid-labile Hg was mixing of fresh water and seawater. Removal of particulate Hg was evident at lower salinities. One-half of the Hg in fresh water appears as a strongly bound form. The strongly bound fraction decreased as salinity increased.

3.2.1. Total Acid-Labile Mercury

The estuarine distribution of total acid-labile Hg is illustrated in Figure 3. The mean and standard deviation (1 σ) for all collections within the estuary was 10 \pm 5 pM. Total acid-labile Hg concentrations were highest at the head of the estuary, in the Providence River decreasing seaward and a high negative correlation with salinity ($r=-.96$) suggests that mixing is an important process in controlling its distribution. However, removal at low salinities was implied by the concentration found

at station 1 (salinity=7.7ppt) which lies significantly below the TDL. In addition, total acid-labile Hg was found to be highly correlated with turbidity ($r = .99$) and total suspended matter ($r = .96$) (see Figure 4a and 4b) indicating that the factors which influence turbidity and suspended load may also be important in the transport of Hg. By deduction, the nonconservative distribution of total Hg was due to the removal of the particulate fraction since dissolved Hg mixed conservatively.

3.2.2. Dissolved Acid-Labile Mercury

The range of dissolved acid-labile Hg concentrations was 17 pM at the tip of the estuary, in the Providence River, to 2 pM, at Station 22 in the Rhode Island Sound. The mean and standard deviation for all collections within the estuary was 7 ± 5 pM. The concentrations measured in situ lie close to the TDL, see Figure 5, and there is a high negative correlation between dissolved Hg and salinity ($r = -.99$) suggesting conservative behavior. This is consistent with the observed conservative mixing for other dissolved trace metals monitored in this survey.

There is evidence in the literature that a portion of trace metals dissolved in river water are removed by flocculation of colloidal matter with increasing ionic strength (Sholkovitz, 1978). Although removal of dissolved Hg during estuarine mixing was not observed in our study of Narragansett Bay it is possible that it was not detected by our sampling scheme. The salinity gradient between 0 and 20 ppt was poorly sampled, as is evident by the scarcity of data for lower salinities in Figure 5. The salinity gradient in the Providence River is sharp and its location variable which makes it difficult

to sample. Significant deviation from the TDL which may have occurred at salinities below 20 ppt would have been undetected. Moreover, removal of trace metals by coflocculation has been shown to occur primarily at salinities less than 15 ppt (op.cit.). Uncertainty in freshwater endmember concentration due to multiple sources and temporal input variability renders placement of the TDL open to error. In addition, the residence time of water in Narragansett Bay is long, calculated to be 40 days at the time of our study, compared to the kinetics of flocculation (less than 1 day). Under these conditions removal of dissolved Hg by coflocculation may have occurred at the tip of the salt intrusion and the resulting mixture was diluted with seawater as it traveled down the estuary.

3.2.3. Particulate Acid-Labile Mercury

As previously mentioned, particulate acid-labile Hg was defined as the concentration measured in the unfiltered collection minus the concentration measured in the filtered collection. The distribution of particulate acid-labile Hg with respect to salinity is plotted in Figure 6. Significant correlation between salinity and particulate Hg was absent although a strong positive correlation with turbidity ($r=.88$) was observed, see Figure 7. Particulate Hg appeared to be removed by settling at low salinities.

3.2.4. Strongly Bound Mercury

The preceding discussion covers the determinations made using the acid digestion procedures. In addition, a strong oxidant was added to the remainder of each unfiltered samples for

reasons stated previously in this paper. Filtered samples were not treated with the bromine monochloride reagent because the entire sample volume was needed for the acid digestion determination. Thermodynamic models predict that all Hg would be converted to a readily reducible form at pH=1, which is achieved with the addition of nitric acid. But models may not accurately represent some ligands present in natural waters, i.e. humic substances. Humic material was found to complex more than 90% of Hg in freshwater (Mantoura, et al., 1978) and there is no information on the breakdown Hg-humic chelates by acid digestion. As previously mentioned, there is evidence that some organic Hg compounds, i.e. CH_3Hg , are not completely recovered by acid digestion.

Compared with the acid digestion, bromine monochloride released additional Hg to unfiltered samples, see Table 4. In general, there was a large increase in the concentration of Hg measured with the addition of the strong oxidant for the river and point source collections. The flow weighted mean fresh water total Hg concentration was calculated to be 78 pM using the cold oxidation determinations. In the estuarine collections the concentration of the strongly bound fraction, as defined in section 2.2.2, decreased dramatically as salinity increased. The strongly bound fraction may have consisted of Hg-humic complexes, an organo-Hg (C-Hg bonds) compound, or Hg complexed with an inorganic substrate on a solid surface. Because the cold oxidation procedure was not conducted on the filtered samples it is impossible to decipher whether the strongly bound Hg existed as a dissolved species or in particulate form. Removal of the

strongly bound fraction during estuarine mixing was indicated by the negative deviation of in situ determinations from the TDL, see Figure 8. Coflocculation with colloidal humic material or hydrous iron oxides is a potential mechanism for the removal of Hg. The strongly bound fraction is a major portion of the fresh water Hg burden and its removal may constitute a significant Hg sink within the estuary.

3.3. Abundances of the Fractions

The abundances of the various fractions were as follows. Dissolved acid-labile Hg constituted 60% of total acid-labile Hg for estuarine collections. Dissolved acid-labile Hg averaged 85% of total acid-labile Hg for riverine water and 50% of point source collections. Particulate Hg averaged 40% of total acid-labile Hg in the estuarine collections, 15% in the river collections, and 50% in the point source collections. The strongly bound fraction averaged 22% in the saline collections. The strongly bound fraction constituted a much larger portion of the Hg in fresh water collection and averaged 55% for river collections and point source collections.

3.4. A Preliminary Mercury Budget for Narragansett Bay

The flux of Hg to Narragansett Bay from various sources has been estimated. These rates, given on Table 5, have been calculated from a single sampling survey and do not account for temporal variability. Although these input rates are not precise, they expose the general magnitude of fluvial and eolian fluxes of Hg to Narragansett Bay. The largest measured fluvial source was the Blackstone River due to, in part, its relatively large flow.

The contribution from the Taunton River was estimated at 22 grams per day assuming a river water Hg concentration of 95 pM which is the average for the four rivers sampled. Fields Point WTF was also a major source largely because of the high Hg content in its effluent. Narragansett Electric, which uses Providence River water for cooling, was not included in the budget because it is not a source of fresh water but rather it is a recycled component.

Tidal flushing results in a net export of Hg from Narragansett Bay. The volume of the tidal prism used was $406 \times 10^6 \text{ m}^3$ (Pilson, 1965). The Hg concentration of incoming Rhode Island Sound water was assumed to be the acid-labile Hg measured at station 22, 5.5pM, resulting in a flood tide flux of 893 grams/day. The export of Hg during ebb tide was calculated at 942 grams/day. It was assumed that the salinity of the outgoing tidal water was 0.2ppt less than the incoming water which is equivalent to the salinity difference between the deep water at Station 22 and Station 13. A fresh water fraction of 1 percent was calculated for the outflowing tidal water. The magnitude of the fresh water fraction is consistent with the residence time of water in Narragansett Bay during low river flow. The entrainment of fresh water increased the Hg concentration of the seawater to 5.8pM assuming an average fresh water concentration of 35 pM for the acid labile fraction (the strongly bound fraction is removed in the estuary). Thus, tidal exchange results in a net export of 49 grams of Hg per day out of Narragansett Bay.

The rainwater flux of Hg to Narragansett Bay was calculated assuming an average concentration of 50 pM (Fogg and Fitzgerald

1979); 328 \cdot km² for the area of the Bay (Pilson, 1985); and 40 inches of rain per year. The magnitude of this deposition emphasizes the importance of atmospheric transport of this volatile constituent. Dry deposition of particulates was estimated to contribute a flux equivalent to 10 percent of the rain water contribution. We were not able to quantify a flux of Hg to Narragansett Bay due to gas exchange.

Removal of mercury due to deposition of the strongly bound fraction was estimated using two assumptions. We assumed, firstly, and as observed that one-half of the total fluvial mercury flux was of a strongly bound form and secondly, that this strongly bound fraction was removed to the sediment. Since the sum of the measured and estimated fluvial sources is 79 grams per day we conclude that approximately 40 g/day would be deposited. The addition of Hg to the water column by remobilization from sediments was not quantified.

Fluvial and atmospheric mercury fluxes listed on Table 5 amount to 89 grams per day while we calculate a net removal of 89 grams per day by tidal flushing and deposition. This preliminary budget suggests that one-half of the Hg entering Narragansett Bay may be removed to the sediments while the remainder mixes conservatively with seawater and is exported by tidal exchange.

3.5. Recent Measurements of Mercury in Estuarine Waters

Some recent measurements of Hg in natural waters are listed in Table 6. The concentration of Hg found in Narragansett Bay was similar to concentrations measured in other estuaries free of major industrial sources of Hg, i.e. Puget Sound, Long Island

Sound, and Gironde River. As expected, the concentration of Hg in Narragansett Bay was an order of magnitude higher than values measured in open ocean waters.

Several studies of the estuarine mixing of dissolved Hg have been conducted. In the Gironde estuary, France, dissolved Hg concentrations were found to decrease seaward and shifted from mostly organic in fresh water to inorganic form in seawater (Figueres, et al., 1985). It was not clear whether this was due to removal of the organic fraction or conversion to an inorganic form. Gill, 1980, studied the Connecticut River estuary and found dissolved Hg to be removed below 13 ppt salinity. The concentration of Hg increased above 13 ppt salinity. Gill suggested that this increase was due to remobilization of flocculated Hg, due to the affinity of Hg for Cl^- species.

4. Conclusion

In our study of Hg in Narragansett Bay, the concentration of Hg decreased seaward of major sources at the head of the estuary. A linear trend between total acid-labile Hg and turbidity may exist, indicating particles and colloidal matter are important vehicles in the estuarine transport of Hg. Removal of Hg in the estuary was evident and was due to settling of particulate Hg. Dissolved acid-labile Hg exhibited conservative behavior but removal during estuarine mixing may have gone undetected.

Compared to acid digestion, cold oxidation of unfiltered samples with bromine monochloride released additional Hg. This additional Hg was strongly bound and may represent organo-Hg associations such as humic chelates, C-Hg bonded organo-mercury

compounds (i.e. CH_3Hg^+), or complexes with an inorganic substrate on a solid surface. It was not ascertained if the strongly bound Hg existed in solution or associated with particulate matter. The strongly bound fraction was present primarily in fresh water and appeared to be removed with increasing salinity.

Further research is necessary to determine the nature of the strongly bound fraction and its role in the transport of Hg. Clearly, the next step must be to reveal whether the strongly bound Hg is of dissolved or particulate form. Additional experiments will be necessary to evaluate the influence of estuarine mixing on the fate of riverine dissolved Hg. For example, the conversion of dissolved Hg to particulate form can be examined in laboratory mixing experiments.

References

- Bloom, N. S. & Crecelius, E. A. 1983 Determination of mercury in seawater at sub-nanogram per liter levels. *Marine Chemistry* 14, 49-59.
- Figueres, G., Martin, J. M., Meybeck, M. & Seyler, P. 1985 A comparative study of mercury in the Tagus estuary (Portugal) and major french estuaries (Gironde, Loire, Rhone). *Estuarine and Coastal Shelf Science* 20, 183-203.
- Fitzgerald, W. F. 1979 Distribution of mercury in natural waters. In *The Biogeochemistry of Mercury in the Environment* (Nriagu, J. O., ed.). Elsevier/North-Holland Biomedical Press, Amsterdam. pp.161-173.
- Fogg, T. R. & Fitzgerald, W. F. 1979 Mercury in southern New England coastal rains. *Journal of Geophysical Research* 84, 6987-6989.
- Gill, G. A. & Fitzgerald, W. F. 1987 Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. *Marine Chemistry* 20, 227-243.
- Gill, G. A. 1980 Mercury geochemistry in Long Island Sound: analytical and field study. M.S. Thesis, Univ. Connecticut.
- Mantoura, R. F. C., Dickson, A. & Riley, J. P. 1978 The complexation of metals with humic materials in natural waters. *Estuarine and Coastal Marine Science* 6, 387-408.
- Olafsson, J. 1982 An international intercalibration for mercury in seawater. *Marine Chemistry* 11, 129-142.
- Pilson, M. E. Q. 1985. On the residence time of water in Narragansett Bay. *Estuaries* 8, 2-14.
- Sholkovitz, E.R. 1978 The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co, and Cd during estuarine mixing. *Earth and Planetary Science Letters* 41, 77-86.
- Sholkovitz, E. R. 1976 Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochimica et Cosmochimica Acta* 40, 831-845.

Table 1

**Acid-Labile Mercury Concentrations in Rivers and Point Sources
Which Contribute to the Providence River**

<u>Source</u>	<u>Total Hg*</u>	<u>Dissolved Hg</u>	<u>Particulate Hg</u>
Rivers			
Woonasquatucket	29pM	26pM	3pM
Blackstone	25	12	13
Moshassuck	8	24	-
Pawtuxet	16	18	-
Point Sources			
Blackstone Valley WTF	34	14	20
Field's Point WTF	252	68	184
East Providence WTF	76	24	52
Narragansett Electric	24	39	-

* Total Hg = Hg determined by acid digestion in unfiltered samples

Table 2
Concentration of Acid-Labile Mercury
in Waters of Narragansett Bay

<u>Station#</u>	<u>Depth</u>	<u>Salinity</u>	<u>Total Hg*</u>	<u>Dissolved Hg</u>	<u>Particulate Hg</u>
	meters	ppt	pM	pM	pM
B01	0.2	7.7	18.5	17	1.5
B02	0.1	21.7	12	7	5
B02	13	29.7	10.5	6	4.5
B04	0.3	24.8	15	6.5	8.5
B04	13.3	30.4	19	3.5	15.5
B05	0.3	27.8	9	5.5	3.5
B05	12.7	29.7	11	6.5	4.5
B07	0.5	28.8	6	5.5	0.5
B11	0.3	20.9	6	3	3
B13	0.4	29.6	6	4.5	1.5
B17	0.3	27.7	15.5	6	9.5
B22	0.9	32.3	5.5	2	3.5
		AVERAGE	<u>11.2±5</u>	<u>6±3.8</u>	<u>5.1±4.2</u>

* Total Hg = Hg determined by acid digestion in unfiltered samples

Table 3

Calculation of Flow Weighted Fresh Water Endmember¹
April 7 - 10, 1986

<u>Source</u>	<u>Flow Rate</u> m ³ /sec	<u>% of Flow</u>	<u>Total Hg²</u>	<u>Dissolved Hg</u>
Blackstone Valley WTF	1	1.8	0.7	0.3
Field's Point WTF	2.7	4.8	13	3.4
East Providence WTF	0.4	0.7	0.8	0.2
Narragansett Electric	8.9	15.8	3.8	6.2
Woonasquatucket River	2	3.6	1.2	1
Blackstone River	28	49.7	13	6
Moshassuck River	2.9	5.2	0.4	1.2
Pawtuxet River	10.4	18.5	2.9	3.2
			-----	-----
		SUM	35pM	22pM

¹ based on acid-labile concentrations

² Total Hg = Hg determined by acid digestion in unfiltered samples

Table 4

Concentration of Mercury in Unfiltered Collections:
Comparison of Cold Oxidation and Acid Digestion Determinations

<u>Source</u>	<u>Cold Oxidation</u>	<u>Acid Digestion</u>	<u>Strongly Bound Fraction</u>
Rivers			
Woonasquatucket	146pM	29pM	117pM
Blackstone	36	25	11
Moshassuck	150	8	142
Pawtuxet	47	16	31
Point Sources			
Blackstone Valley WTF	94	34	60
Field's Point WTF	346	252	184
East Providence WTF	135	76	59
Narragansett Electric	42	24	18
Estuarine Stations			
B01 (7.7ppt)	26	19	7
B04 (24.8ppt)	19	15	4
B05 (27.8ppt)	11	9	2

Table 5

Sources and Sinks of Mercury
in Narragansett Bay
(Preliminary Budget)

	<u>Flux(grams/day)</u>
Rivers	
Blackstone	17.5
Moshassuck	7.5
Woonasquatucket	5
Pawtuxet	8.5
Taunton	22 ^a
Point Sources	
Blackstone Valley WTF	1.6
Field's Point WTF	16
East Providence WTF	0.9
Atmospheric Sources	
Dry Deposition (particulates)	0.1 ^b
Gas Exchange	?
Rain	10
	<hr/>
Net Input	+89
Tidal Exchange	-49
Deposition	-40 ^a
	<hr/>
Net Removal	-89

^a estimate, see text Section 3.4

^b estimated at 10% of rain, see text Section 3.4

Table 6

Recent Measurements of Mercury In Natural Waters

<u>Location</u>	<u>Total Hg</u>	<u>Reference</u>
N. Pacific (open ocean)	1.6±.3 pM	Gill and Fitzgerald, 1987
Gironde Estuary (France)	15-30 (dissolved)	Figueres, et al., 1985
Long Island Sound	30±6	Gill, 1980
Puget Sound	5	Bloom and Crecelius, 1983
Rain (S. New England)	50±25	Fogg and Fitzgerald, 1979
Narragansett Bay	10±5	This Work

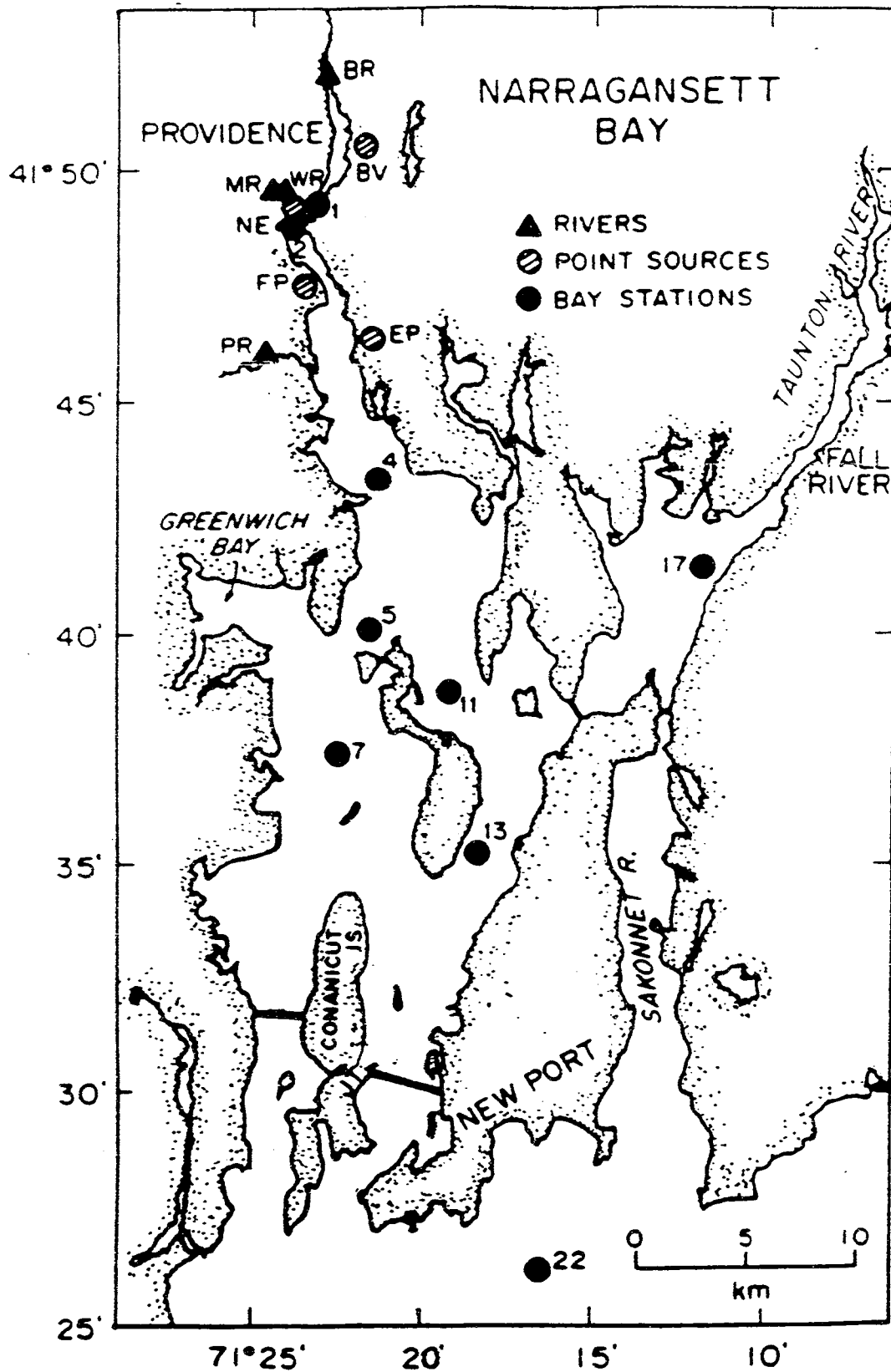
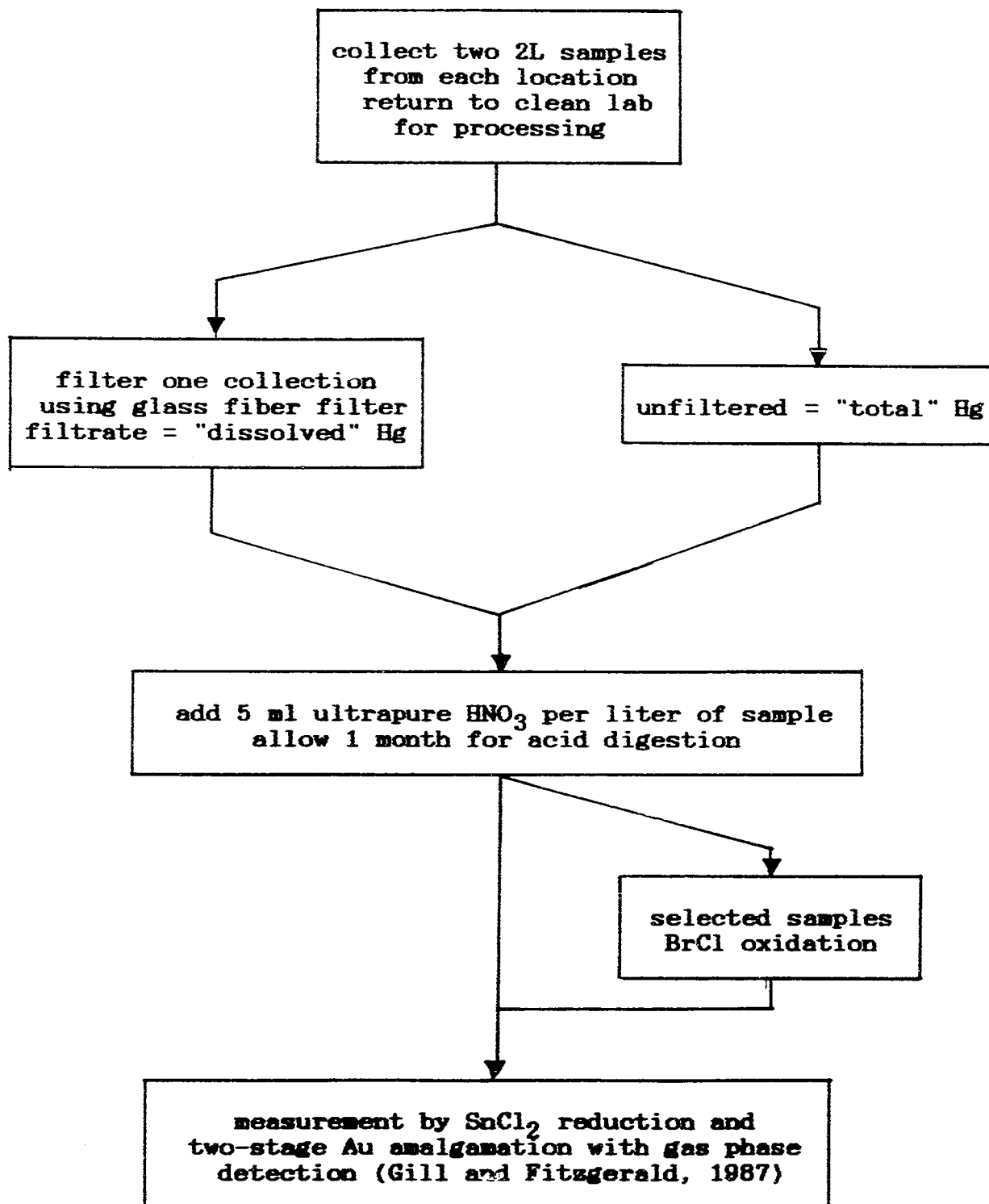


Figure 1

**Station Locations for Narragansett Bay Synoptic Survey
 (reprinted from Narragansett Bay Water Quality Monitoring and
 source Strength Measurements: cruise and data report, URI, 1985)**

Figure 2

Flow Diagram of Experimental Procedure



Narragansett Bay
Western Passage (surface)

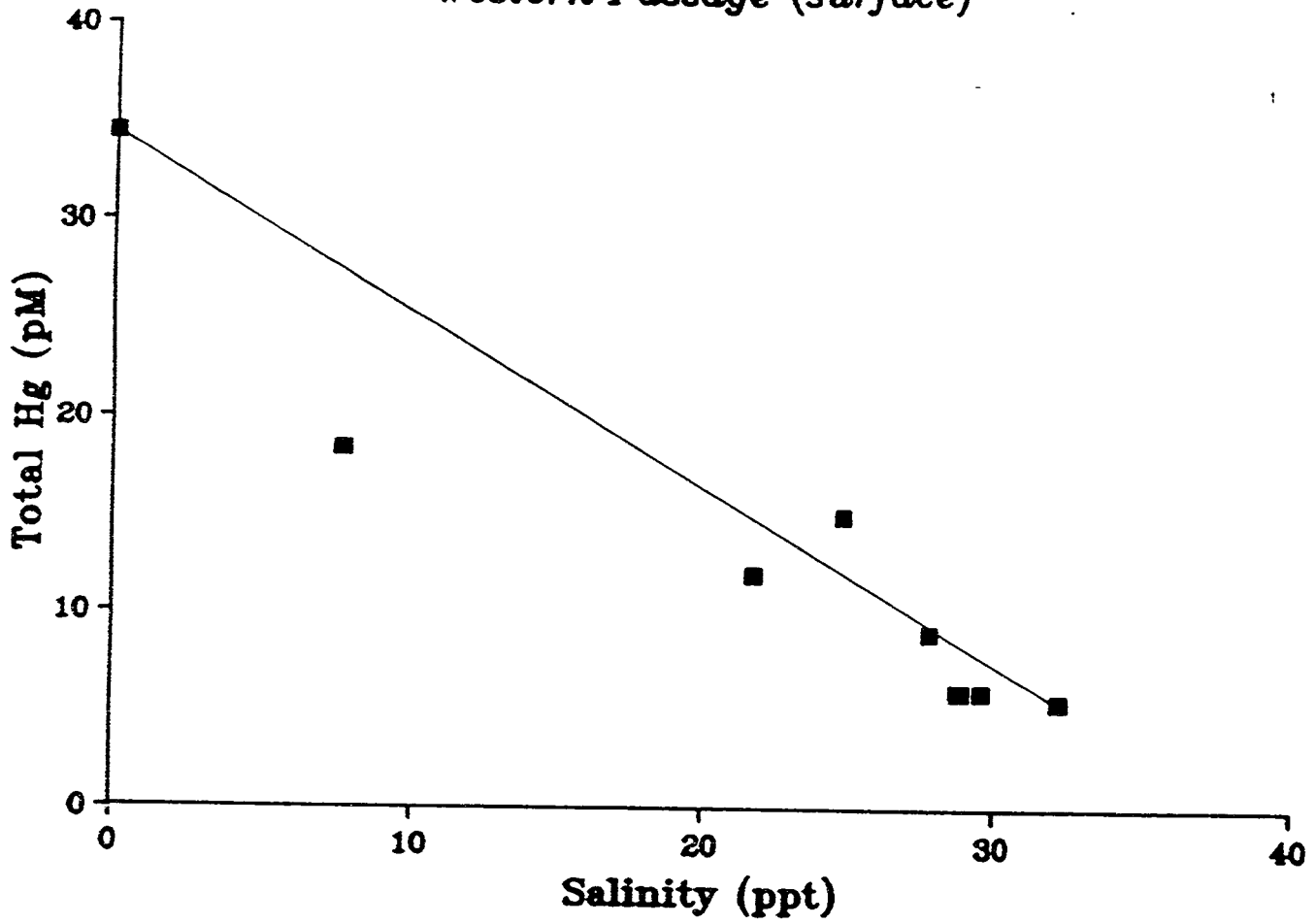


Figure 3

Distribution of Total Acid-Labile Hg versus Salinity

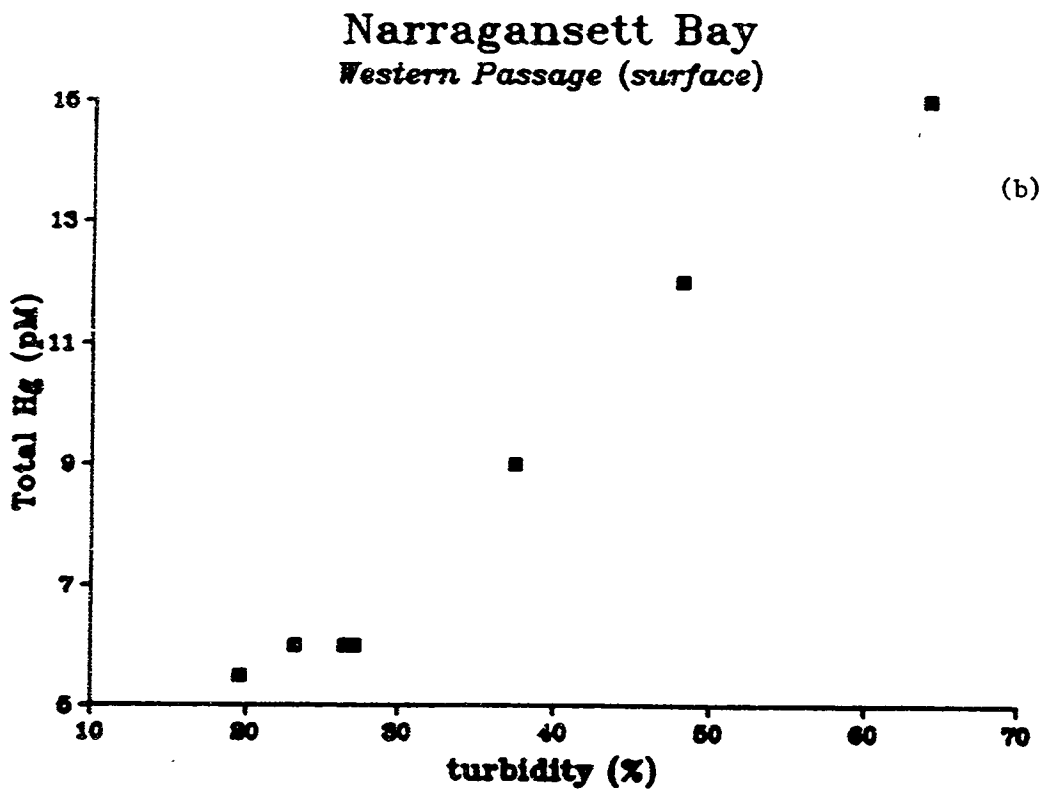
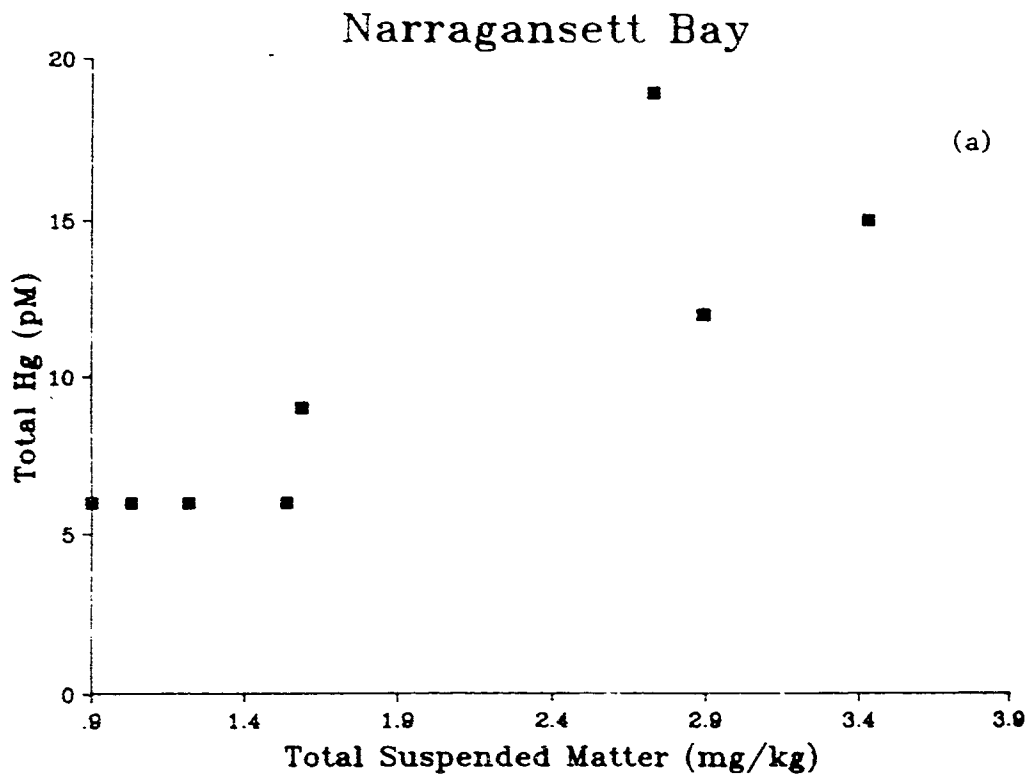


Figure 4

Distribution of Total Acid-Labile Hg versus
Total Suspended Matter (a) and Turbidity (b)

Narragansett Bay Western Passage (surface)

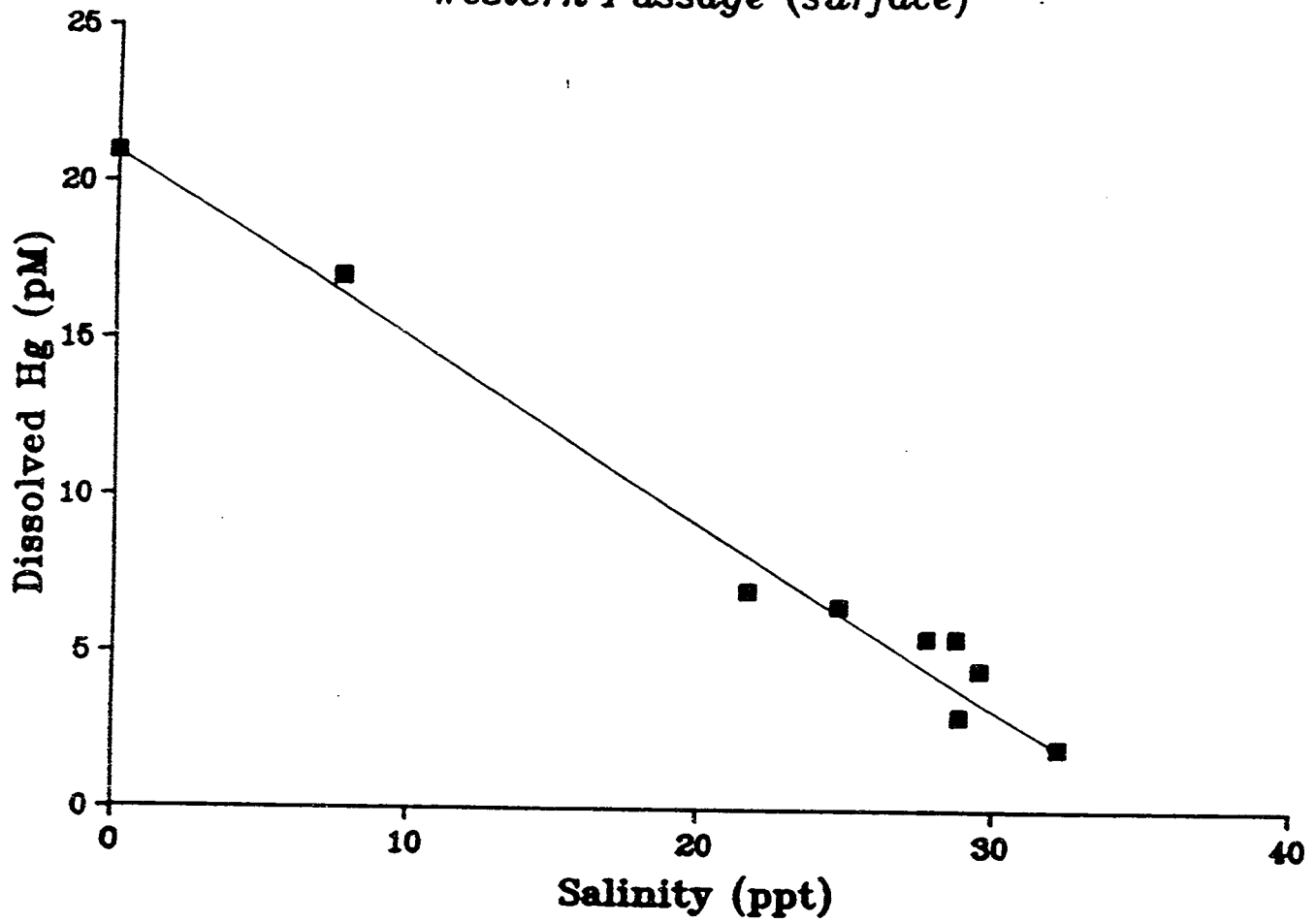


Figure 5

Distribution of Dissolved Acid-Labile Hg versus Salinity

Narragansett Bay
Western Passage (surface)

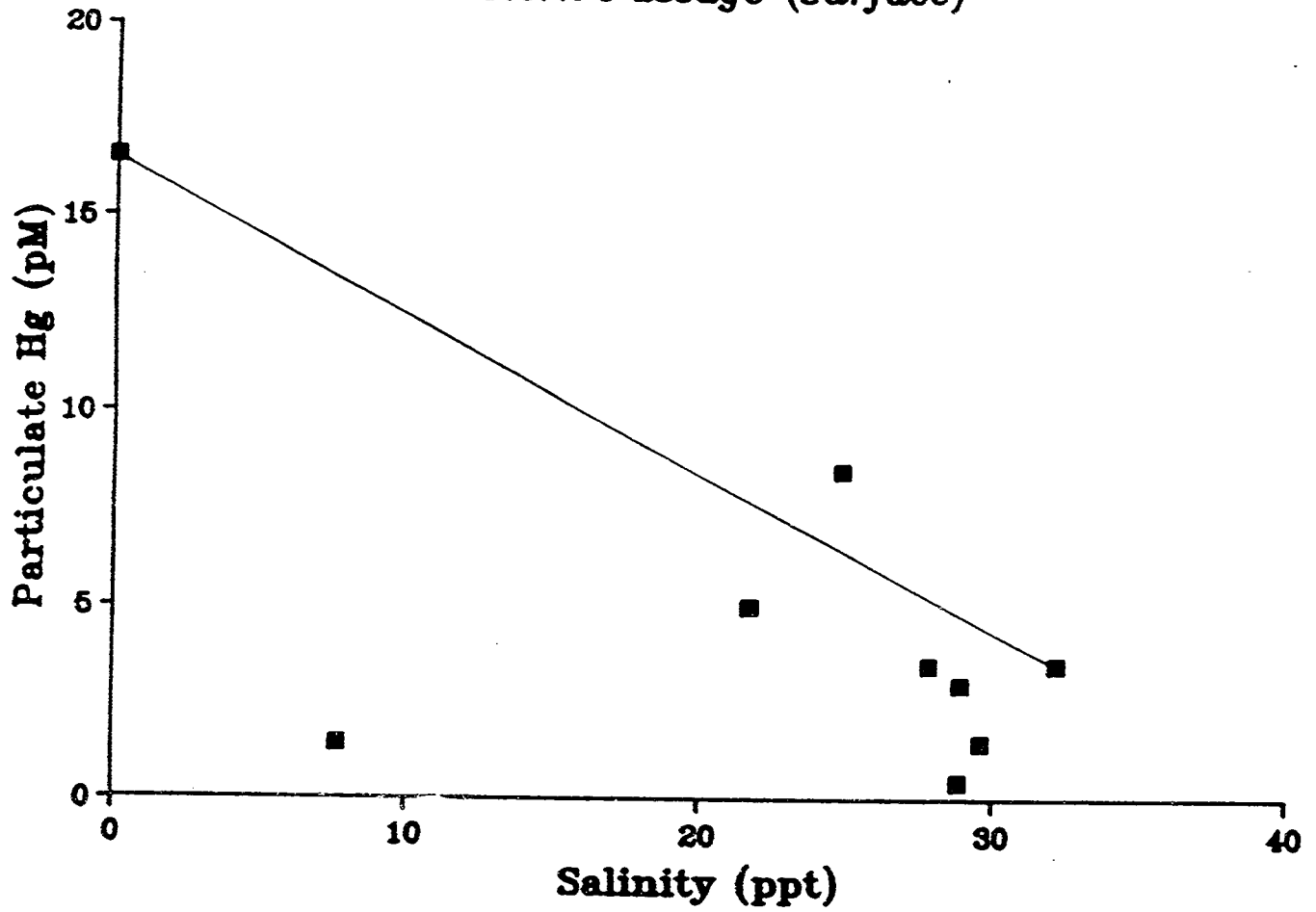


Figure 6

Distribution of Particulate Acid-Labile Hg versus Salinity

Narragansett Bay Western Passage (surface)

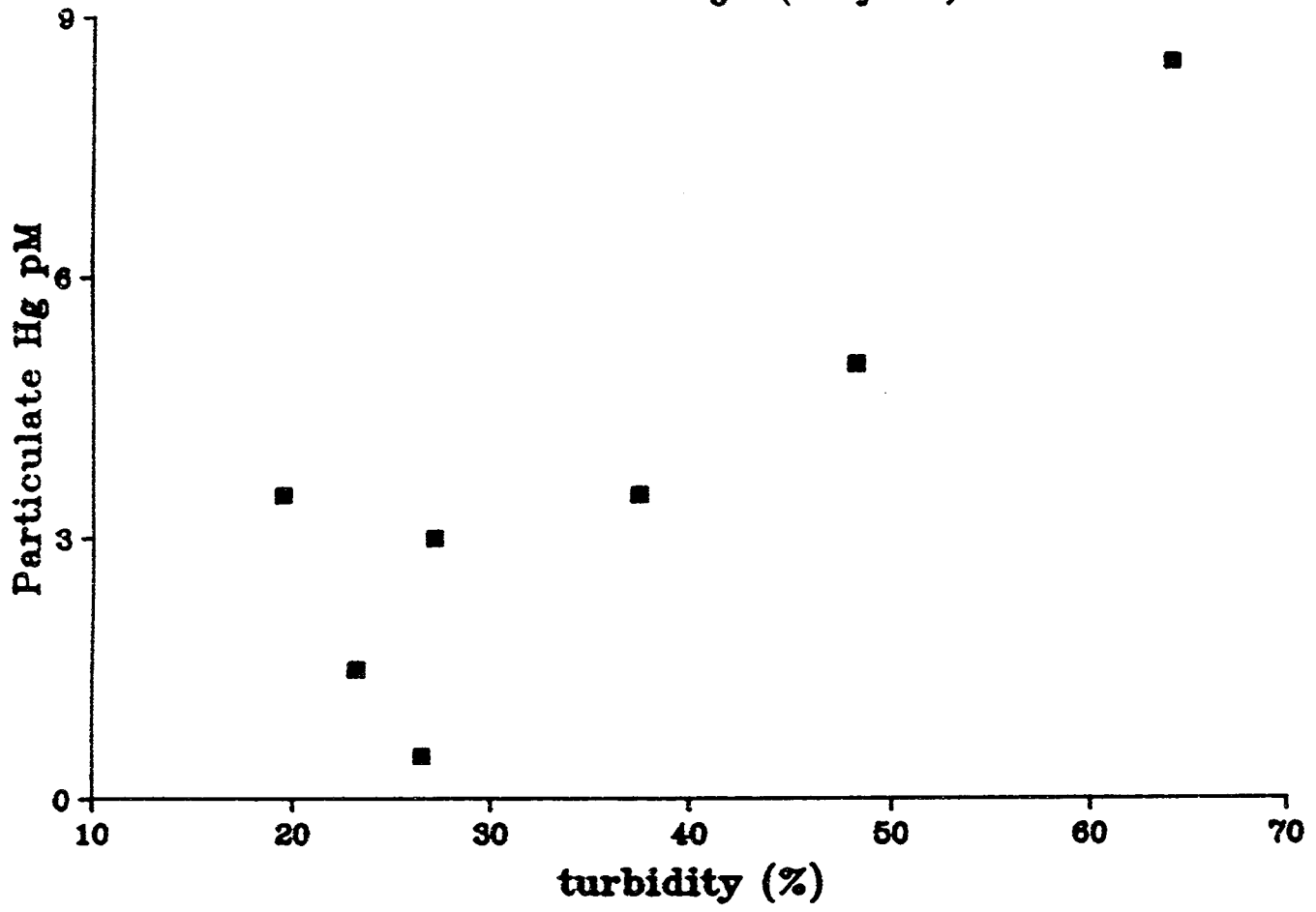


Figure 7

Distribution of Particulate Acid-Labile Hg versus Turbidity

Narragansett Bay
Strongly Bound Fraction

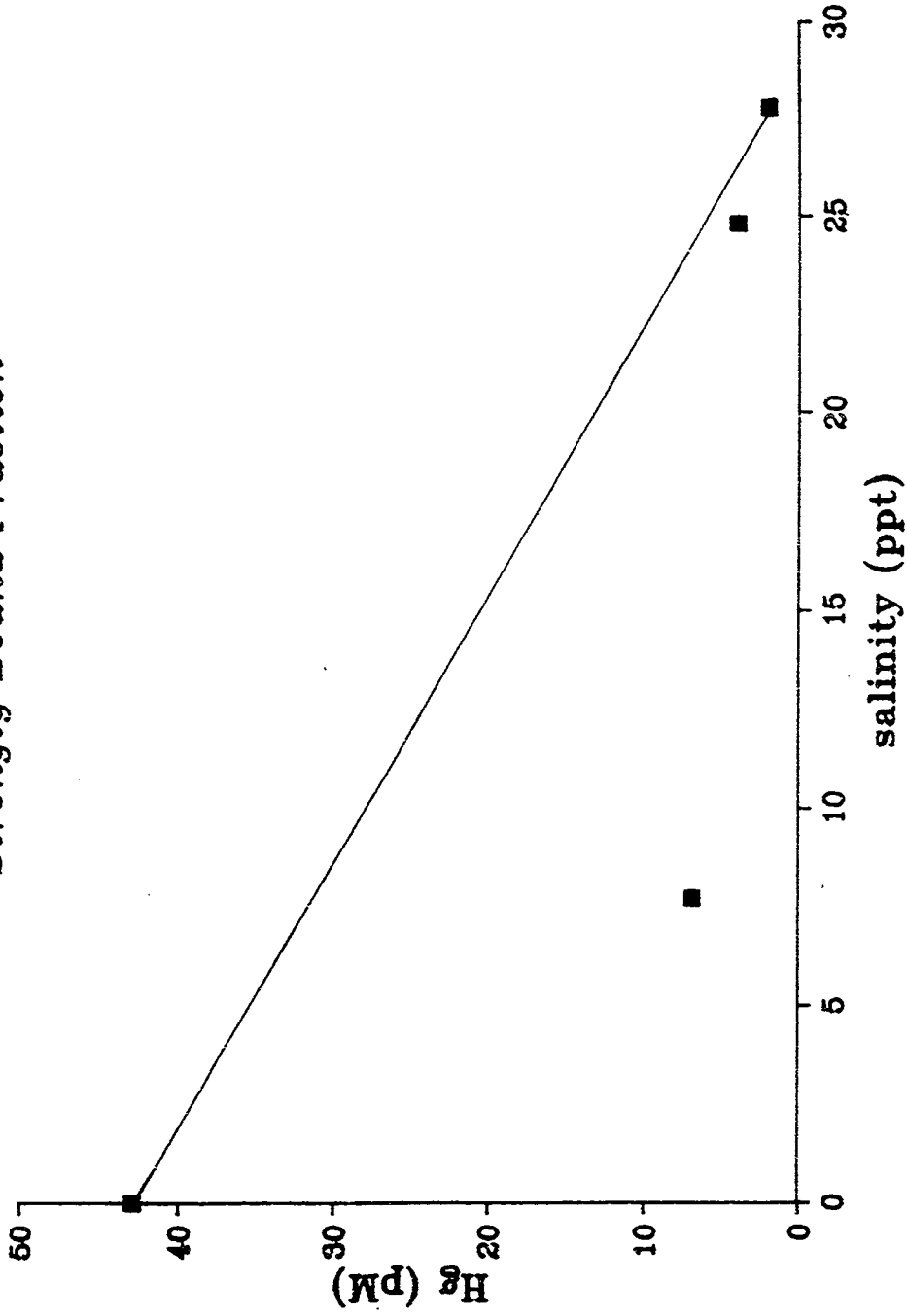


Figure 8

Distribution of Strongly Bound Hg versus Salinity