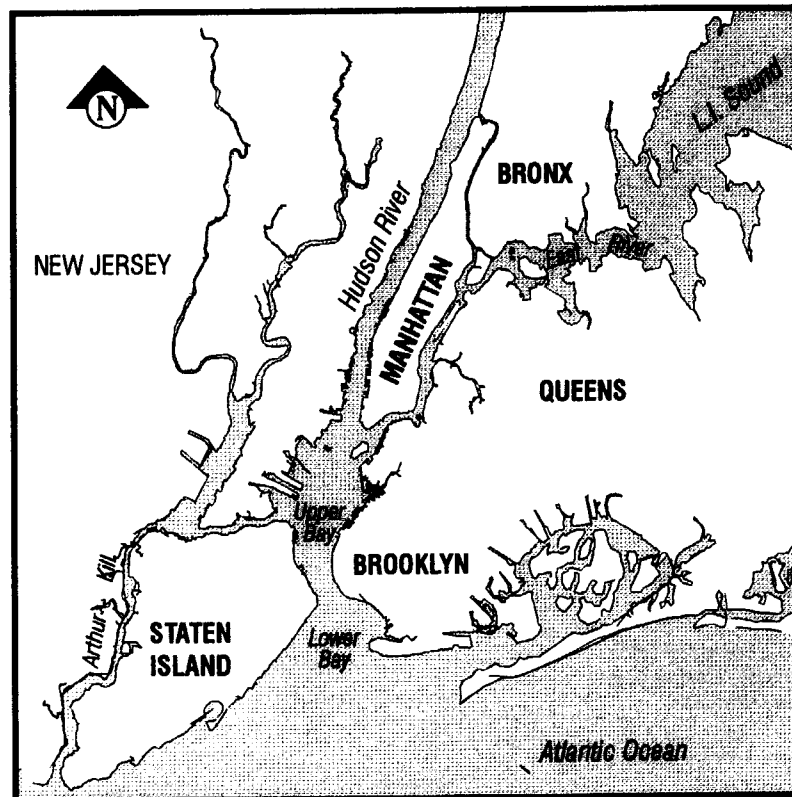


**U.S. Environmental Protection Agency, Region II  
New York/New Jersey Harbor Estuary Program  
Water Management Division  
Surface Water Quality Branch**

**Development of  
Total Maximum Daily Loads  
and Wasteload Allocations  
for Toxic Metals in NY/NJ Harbor**

**Modeling Report**

**September, 1995**



**HydroQual, Inc.**  
Environmental Engineers and Scientists

**U.S. Environmental Protection Agency, Region II  
New York/New Jersey Harbor Estuary Program  
Water Management Division  
Surface Water Quality Branch**

**DEVELOPMENT OF TOTAL MAXIMUM DAILY  
LOADS AND WASTELOAD ALLOCATIONS  
FOR TOXIC METALS IN NY/NJ HARBOR**

**MODELING REPORT**

**Job Number: TETRO103**

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**September 1995**

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## SUMMARY OF FINDINGS

1. The accurate measurement of trace metals in ambient waters requires the utilization of state-of-the-art "clean" analytical techniques. Historical measurements of trace metals are probably not accurate, and can differ erratically from modern day measurements by at least an order of magnitude.
2. In New York/New Jersey Harbor total recoverable metal is approximately equal to both acid soluble metal and the arithmetic sum of dissolved and particulate metal for the trace metals copper, mercury, nickel, lead, silver, arsenic, cadmium, and zinc.
3. Instantaneous observed concentrations of mercury, nickel, and lead were apparently in excess of the respective numeric criteria adopted for the New York/New Jersey Harbor Wasteload Allocation (WLA) during at least one of the three ambient metals surveys. Based on observed data, the following waterbodies exceeded water quality criteria.

<u>Mercury</u>	<u>Nickel</u>	<u>Lead</u>
Hudson River	Hudson River	Hudson River
East River		Kills
Inner Harbor		
Raritan Bay		
Kills		
Jamaica Bay		
Hackensack River		
Passaic River		
Newark Bay		

4. Total recoverable metals concentrations in New York/New Jersey Harbor vary over the tidal cycle at certain locations. This variability is coincident with variations in

suspended solids concentrations. The effect of the tidal cycle on concentrations of dissolved metals, however, is relatively negligible; the concentrations are approximately constant. Thus, the impact of tides on ambient concentrations of metals in New York/New Jersey Harbor is related only to the metal particulate fraction.

5. During both the January 6 through 12, 1991, and the October 28 through 31, 1991 monitoring periods, there did not appear to be appreciable net deposition of particulate metal from the water column to the sediment bed. The total metal concentration for these surveys balanced as a conservative variable. The January and October surveys are representative of "above average" and "low" flow conditions, respectively. It is recognized that the study did not capture a truly "high" flow event and that a metals balance on a yearly basis may not be conservative. Future studies should consider monitoring the ambient waters for metals during and after a "high" flow event.
6. On a regional basis, concentrations of dissolved and particulate metals are log normally distributed. Regional log probability distributions of total recoverable metals may be approximated by constructing the probability distribution of the arithmetic sum of dissolved and particulate metals concentrations.
7. Variability observed in concentrations of dissolved metals, which is not strongly correlated to tidal cycle position, may be interpreted as the variability which would be observed in particulate metals if no tides were present. This non-tidal variability in harbor metals may be attributed to hydrodynamic variations, loading variations, and analytical errors in sample collection and processing.
8. To perform wasteload allocations based on the criteria developed for chronic toxicity, only the non-tidal variability is considered. Chronic criteria is based on one exceedance in three years of 4-day average concentrations.

9. Applying adopted criteria to the data collected in the eight regions of the study area on a chronic toxicity dissolved basis for copper, and on a chronic toxicity total recoverable basis for the other seven metals, exceedances of criteria for copper, mercury, nickel, and lead are projected. Projected exceedances are calculated for the following waterbodies.

<u>Mercury</u>	<u>Nickel</u>	<u>Lead</u>	<u>Copper</u>
Hudson River	Hudson River	Kills	Raritan Bay
Raritan Bay	Kills		
Kills			
Jamaica Bay			
Hackensack River			
Passaic River			
Newark Bay			

10. Limited water column metals data collected at headwater locations in the Hackensack, Passaic, and Raritan Rivers are indicative of perhaps more extensive criteria contamination in the New Jersey tributaries than indicated by the 1991 survey data. Additional data collection efforts in these locations is recommended.
11. Data collected during February 1992, a winter period, in the sediments of the study area indicate that the acid volatile sulfide concentrations are sufficient enough to bind observed molar sums of simultaneously extracted metals. Acid volatile sulfide levels in sediments vary temporally, and are typically at their lowest in winter months. Hence, it is unlikely that the bed sediments act as a source of metals to the water column for the metals of concern, with the possible exception of mercury.
12. The steady state model framework developed for the WLA effort is satisfactorily calibrated with observed data for seven of the eight metals of concern for both the

January "above average" flow and October "low" flow conditions using loadings as agreed upon by USEPA Region II and the states of New York and New Jersey.

13. Model calibration for mercury for both the January and October calibration periods could not be achieved without the utilization of a source input of unknown origin. The unknown source is nearly 20 times greater than the known point source load. It is hypothesized that this unknown source may originate from atmospheric deposition and/or methylation of sediment mercury. Further efforts are required to define this source.
14. Observed headwater input concentrations for copper, nickel, and lead are sometimes greater than the proposed respective criteria. Boundary conditions for the various tributaries to the study area must be set to compliance if remediation scenarios for other sources are to be evaluated. For projections, using the October low flow calibration, boundary conditions are set equal to observed data if the data are less than criteria, and are set equal to criteria if the data are greater than the criteria.
15. Any remediation action proposed for New York/New Jersey Harbor for sources of those metals requiring waste load allocation may have both interstate and interregional consequences. For this reason, it is advisable to develop source remediation scenarios using the WLA model framework on a system-wide basis. To facilitate source remediation projections of ambient water quality, unit response matrices have been developed for the metals copper, mercury, nickel, and lead. The linearity of the WLA model equations allows for the development of the unit response matrices.



## SECTION 1

### INTRODUCTION

Under the provision of Section 304(l) of the Clean Water Act, the waters of New York/New Jersey Harbor have been short listed for the metals copper and mercury. Historical ambient copper and mercury concentrations were found to violate the most stringent of ambient criteria as set forth by either of the states of New York and New Jersey or the U.S. Environmental Protection Agency (EPA). Preliminary calculations also indicated that the violations of ambient criteria for copper and mercury may be solely attributed to discharges from point sources. In addition to the metals copper and mercury, six other heavy metals were identified as potential toxicants in the Harbor. These metals include arsenic, cadmium, nickel, lead, silver, and zinc. In accordance with the Clean Water Act, the short listing of New York/New Jersey Harbor for copper and mercury ambient criteria violations mandates that the permits of dischargers to New York/New Jersey Harbor be revised so that ambient criteria are not contravened.

To achieve the required revisions of permits for dischargers to New York/New Jersey Harbor, total maximum daily loads (TMDL) allowable for the metals copper and mercury to the waters of the Harbor were determined, and a method for allocating these loads among the dischargers was established. The waste load allocation (WLA) effort for the metals copper and mercury was jointly managed by the states of New York (NYSDEC) and New Jersey (NJDEPE) and EPA Region II under the auspices of the Harbor Estuary Program (HEP).

The waste load allocation effort required extensive measurement of ambient concentrations of metals in the harbor. Table 1-1 summarizes the data monitoring programs conducted as part of this TMDL/WLA effort. The harbor metals database had to be both spatially and temporally expansive, as concentrations of metals in New York/New Jersey Harbor are not constant over space or time. The waters of New York/New Jersey Harbor originate from diverse drainage basins and are markedly influenced by upstream freshwater and saline ocean inputs. The influence of the ocean

and upstream boundaries on the Harbor varies temporally, and is dependent upon many hydrodynamic, hydrologic and climatological factors. Further variability is associated with local tidal cycle events. Only with an extensive knowledge of the conditions existing in the Harbor could a modeling framework be developed which would be adequate to support the development of a technically defensible waste load allocation.

TABLE 1-1. MONITORING PROGRAMS FOR THE TOXIC METALS TMDL/WLA

Title	Stations	Frequency	Parameters	Forms <sup>b</sup>	Comments
January 1991 Ambient Survey	37, TB <sup>a</sup>	Once	Ag, As, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR, D, P, AS	7 stations used for inter- lab comparison
January 1991 Municipal Survey	21	Once	Ag, As, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR, D, P, AS	14 municipals used for inter- lab comparison
May 1991 Intensive Ambient Master Station Survey	6	4/tidal cycle	Ag, As, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR, D	-
October 1991 Low Flow Ambient Survey	18 TB <sup>a</sup>	Once	Ag, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR, D	-
February 1992 Sediment Survey	20	Once	8 metals, whole sediment, pore water, DOC, SEM, AVS	TR	Toxicity bioassays also performed
Tributary Monitoring	4	6	Ag, As, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR, D	
CSO Monitoring	17	1-2	Ag, Cd, Cu, Hg, Ni, Pb, Zn, TSS, PC, POC	TR	10 stations are NYC wet weather influent
<sup>a</sup> TB	= Top and bottom				
<sup>b</sup> TR	= Total Recoverable				
D	= Dissolved				
P	= Particulate				
AS	= Acid Soluble				

Further data requirements of the waste load allocation effort pertain to the sources of the toxic metals themselves. The waste load allocation process is based on the assumption that all loads have been accurately accounted for. Thus, it was necessary to sample sewage treatment plant (STP) effluents, combined sewer overflow (CSO) outfalls, and wet weather STP influents. It was equally important to characterize all harbor boundaries, including tributaries, ocean, upstream, and bed sediment.

This report is a detailed account of the development of a technically defensible basis for development of a waste load allocation for the metals copper, mercury, nickel, lead, silver, arsenic, cadmium, and zinc. The waste load allocation effort can be conveniently categorized into four operational areas: data collection and analysis, evaluation of target concentrations, model development and calibration, and model projection.

## SECTION 2

### DATA COLLECTION AND ANALYSIS

#### 2.1 REVIEW OF HISTORICAL DATA

The database collected by the New York City Department of Environmental Protection (NYCDEP) as part of the routine Harbor Survey program was readily available to define ambient concentrations of metals in New York/New Jersey Harbor. The Harbor Survey involves the sampling of 52 stations located within New York/New Jersey Harbor on a regular basis. Figure 2-1 shows the spatial coverage of the Harbor Survey. In addition to water column metals, the Harbor Survey also includes solids, salinity, and sediment metals among numerous other quality variables.

Harbor Survey data collected over the period 1974 through 1988 for the metals copper, mercury, cadmium, lead, nickel, and zinc were evaluated. Also reviewed were silver data collected during 1986 and 1988. The Harbor Survey data are measures of total recoverable metal, that is, the sum of both dissolved metal and particulate metal. Prior to 1986, Harbor Survey metals data were collected annually at each station at two depths during the months June through September. During this time, the two depth samples at each station were composited before analysis. After 1985, each station was sampled twice a month during the four month survey period at two depths. Thus, for each station 16 samples were obtained. All samples at each station were composited before analysis. The compositing procedure was depth selective; however, for 1987, surface and bottom samples were composited together before analysis. The data obtained from NYCDEP were reported as means of top and bottom composites for the years 1986 and 1988, and as a single composite value for 1974 through 1985 and 1987. The sampling frequency, compositing method, and reporting method are detailed in Table 2-1.

TABLE 2-1. NYCDEP HARBOR SURVEY SAMPLE COLLECTION, PROCESSING, AND REPORTING METHODS FOR WATER COLUMN TOTAL RECOVERABLE METALS AT GIVEN STATION

Year	Sampling Frequency	# Depths Per Station	Compositing Method	# of Lab Analyses	Reported Value
1974-1985	1	2	all samples	1	as measured
1986	8	2	depth selective	2	mean of top and bottom laboratory measures
1987	8	2	all samples	1	as measured
1988	8	2	depth selective	2	mean of top and bottom laboratory measures

The review of the Harbor Survey water column metals data consisted of both temporal and spatial analyses. Temporal analysis of the data was performed in two ways: for each metal at each station and for each metal at station groups. Metals data at each station were plotted as a function of the year of their collection for each metal. These plots show that concentrations of all of the metals considered vary dramatically and erratically over time. Reported concentrations of ambient water column metals from 1974 to 1988 increase and decrease sporadically. Further temporal analysis was performed by grouping Harbor Survey stations by area. For example, Hudson River, East River, Inner Harbor, etc. For each metal, data plots were constructed such that area-wide concentration ranges over the time period were observed. Again the variation in metals concentrations were large and sporadic, both within a given year and among years. Such dramatic changes in metals concentrations over long-term time periods could be indicative of quality control problems inherent within data sampling and processing procedures.

Spatial analysis of the data also was also performed. Data plots in which temporal ranges of the data were presented along spatial transects showed relatively little variability for each metal across transects. Grouping data across longitudinal transects to derive area average concentrations for each metal resulted in even less spatial variation of the data.

Averages obtained from areas with presumably different characteristics were similar. Figure 2-2 illustrates the average concentration for eight major water bodies in the Harbor. Figure 2-2 also compares the reported concentrations of historic metals to the metals criteria used by EPA Region II for New York/New Jersey Harbor. A tabulation of the criteria may be found in Table 2-2. The copper value of 5.6  $\mu\text{g/L}$  was derived from a site-specific criteria investigation in New York/New Jersey Harbor as part of this study. The data suggest severe contravention of all criteria over almost the entire survey area.

Metal	Criterion ( $\mu\text{g/l}$ )	Phase	Compliance Frequency
Cu	5.6	dissolved	chronic
Hg	0.025	total recoverable	chronic
Ni	7.1	total recoverable	chronic
Pb	8.5	total recoverable	chronic
Ag	0.92	total recoverable	chronic
As	36	total recoverable	chronic
Cd	2.7	total recoverable	chronic
Zn	58	total recoverable	chronic

Sediment metals data available for cadmium, copper, lead, mercury, nickel, and zinc from 1983 to 1989, and silver from 1989 were analyzed in the same manner as described above for the water column data. The sediment data is characterized by more consistent temporal trends than the water column data on both a station by station and an area average basis. Sediment metals also show strong gradients along longitudinal transects. The sediment metals data seem to reflect that different areas of the harbor are subject to different loadings of metals, and that certain areas within the harbor are zones of sediment accumulation. Figure 2-3 contains a summary of the spatial differences in metals concentrations among sediments from different areas of New York/New Jersey Harbor.

The full spatial and temporal analyses of the NYCDEP Harbor Survey data are contained in Appendix I. Further information on Harbor Survey data may be obtained from New York Harbor Water Quality Survey: 1988 - 1990 (NYCDEP 1991).

The water column metals data collected by the NYCDEP Harbor Survey agree well with other sets of historical water column metals data. These data, however, do not agree with water column metals data collected in New York/New Jersey Harbor by EPA in the July 1988 Anderson cruise. In general, metal concentrations from the July 1988 cruise were considerably lower than the historical measurements. It is also noted that the July 1988 cruise used "clean" sampling and measurement techniques. The disparity between historical data and the July 1988 data raised the question of possible contamination with historical data sets.

The analysis of historical data raised many issues relative to the waste load allocation. The most immediate issues which were addressed include:

- are the historical data valid, and should these data be used for calibration of the waste load allocation modeling framework?
- what is(are) the most appropriate metal phase(s) to measure and what is (are) the most appropriate metal phase(s) for water quality standards?

## **2.2 JANUARY 1991 AMBIENT SURVEY AND MUNICIPAL MONITORING**

To address the issues raised by the review of historical ambient metals data, the HEP organized an ambient water column and municipal effluent study. One purpose of this study was to create an inter-laboratory comparison. The comparison made was between the collection and analytical techniques of Battelle Ocean Sciences, a laboratory which was equipped to measure metals concentrations at the levels detected during the Anderson cruise, and the NYCDEP Harbor Survey, the major source of historical metals data in New York/New Jersey Harbor. Also included in the comparison study were the laboratories

which normally handle municipal effluent monitoring, including representation from New York State, New York City, New Jersey, and Westchester County. The study included seven sampling stations in the harbor and 21 sewage treatment plants. The seven stations for the inter-calibration study are shown on Figure 2-4. In addition to the seven inter-laboratory sampling stations, Battelle also sampled at thirty other sites in the Harbor. The 37 stations sampled by Battelle are located on Figure 2-5.

The ambient portion of the survey took place from January 6 through 12, 1991. This time period was characterized by heavier than average precipitation and above average flow conditions. Municipal effluent sampling was conducted between December 1990 and February 1991. The study was designed to measure metals in four phases: total recoverable, acid soluble, dissolved, and particulate. Other participants in the study, with the exception of New York State's laboratory, measured metals in only the total recoverable form.

### **2.2.1 Inter-Laboratory Comparison**

The conclusion drawn from the ambient inter-laboratory comparison was that poor agreement existed among the three laboratories. The disparity of results, however, was of substantially smaller magnitude than the discrepancy observed between present day and historic metals measurements. Of particular concern was the comparison between Battelle and NYCDEP. It was hoped that the side-by-side comparison might pinpoint the cause of rather high NYCDEP historic metals measurements. It was also intended that, given a cause, the historic data could be salvaged through the application of a correction factor. Data collected by Battelle and NYCDEP during the inter-calibration study were analyzed so that sampling techniques, laboratory processing, and the ability of one laboratory to perform both collection and processing roles could be directly compared.

Figures in Appendix II show the comparisons between Battelle and NYCDEP for seven metals in the total recoverable form. For each metal, the performance of each laboratory's processing skills are compared. For the laboratory processing skills



comparison, both laboratories were given the opportunity to collect the samples. Similarly, the comparison between the abilities of the laboratories to collect data were evaluated with both laboratories performing the chemistry. The intermediate laboratory comparisons do not show any one weakness for either of the two laboratories. The two laboratories obtained different results for the most part, but no consistent trends exist. Each data set passed quality controls. Of further interest to the HEP was how the January 1991 ambient survey data compared to historical data. Results reported by NYCDEP for the comparison study are much lower than results previously obtained from Harbor Survey cruises.

Split sampling of municipal effluents at 14 STPs were also performed by Battelle and NYCDEP. Discrepancies between the two laboratory measurements were observed. These discrepancies, for both the ambient and municipal sample comparisons, have never been fully resolved, but the differences between NYCDEP and Battelle were not as severe as the ambient historical data would indicate. The results of the split sampling of municipal effluents conducted by Battelle and NYCDEP are also presented in Appendix II.

### **2.2.2 Ambient Water Quality**

The ambient water column metals and hydrographic data collected by Battelle January 6 through 12, 1991, reflect conditions existing in New York/New Jersey Harbor at above average flow conditions; Hudson River flow averaged about 25,000 cfs. For each metal, all four phases measured by Battelle were examined spatially along longitudinal transects tracking major areas of New York/New Jersey Harbor. These results are shown on Figures 2-6 through 2-21. An important conclusion that may be deduced from these data is that, on an overall basis, total recoverable measurements are equivalent to the acid soluble measurements. Therefore, the issue regarding the distinction between these two types of measurements is not necessary. Also the criteria, shown on Table 2-2, are exceeded only by mercury and lead.

Total recoverable mercury contravenes its criterion over almost the entire longitudinal span of the Kills and at single locations in the Hudson, Hackensack, and Passaic Rivers and Newark Bay. The lead criterion exceedance is limited to a sole point in the Arthur Kill on a total recoverable basis.

Another generalization which can be made about the findings of the January ambient survey is that in the vicinity of the junction of the Hudson and Harlem Rivers (Hudson River milepoint 13.5), peak concentrations of total recoverable metal in the lower layer of the Hudson River are observed. This is coincident with a spike in the suspended solids data as Figure 2-22 shows indicating that elevated metals concentrations in the water column may result from resuspension of bottom sediments. To address this issue, three courses of actions were taken: an extensive review of existing Hudson River suspended solids databases, a synoptic survey of water column turbidity, and the organization of another ambient water column survey which would include sampling for metals over the tidal cycle as opposed to the one-time grab samples collected during the January 6 through 12, 1991, ambient survey.

### **2.3 REVIEW SUSPENDED SOLIDS DATA**

The review of Hudson River suspended solids databases included the works of NYCDEP Harbor Survey (1990 and 1991 routine sampling and special tidal cycle surveys), Hirschberg and Bokuniewicz (1980 and 1981, released upon the request of the Hudson River Foundation), Bero (1989 through 1991 for the Hudson River Foundation), Olsen (1975-1977), and the United States Geologic Service, NYDEC, Interstate Sanitation Commission, and EPA Region 2 (period of records found in STORET). Figure 2-23 contains a master plot of the suspended solids from all of the above sources showing the mean and plus or minus one standard deviation of the data available at a particular location in the Hudson River. Individual analyses of the databases over time, depth, and longitudinal space may be found in Appendix III. The Hudson River database shows that elevated solids occur frequently in the Hudson River over a significant distance along the thalweg

