Clean Trace Metal Measurements in the Houston Ship Channel

Paul Jensen, Ph. D., P.E.
Vice President, PBS&J

Dr. Jensen's experience in Galveston Bay includes work as an officer on cargo ships, a graduate student and researcher conducting field data collection, manager for several channel deepening feasibility studies, manager for several water quality studies, and investigator on projects for the Galveston Bay National Estuary Program. He has a Masters in Oceanography and a Doctorate in Environmental Engineering, both from Texas A&M University. He is currently a Vice President with PBS&J, and has been with the same organization since 1979.

CLEAN TRACE METAL MEASUREMENTS IN THE HOUSTON SHIP CHANNEL

Paul Jensen, PBS&J, Austin
Holly Chen, Omega Engineers, Houston
Paul Boothe, Texas A&M University, Trace Element Research Lab, College Station
Charles Marshall, Texas Natural Resource Conservation Commission, Austin
Teresa Battenfield, City of Houston

Since trace metal standards were developed from laboratory data in the mid-1980s, there has been a continuing challenge in making field observations at concentrations as low as the calculated criteria. Over the years attempts to measure the very low concentrations required have been plagued by analytical difficulties and contamination problems, particularly in dealing with estuarine samples. Because of these problems, historical metals data (data from the 1970s and 80s) have been shown to have major problems, with values orders of magnitude higher than are measured with modern methods. The technology to obtain reliable observations has been slowly evolving over the last decade, and is still relatively rare and costly. As a result, there are still relatively few accurate observations of trace metals that can be reliably compared with ambient criteria.

Recognizing the need for accurate data, the Texas Clean Rivers Program, administered in the area by the Houston-Galveston Area Council (H-GAC), worked with the City of Houston, the TNRCC and the Texas A&M University Trace Element Research Laboratory (TAMU-TERL), to obtain an additional set of 24 samples from the Houston Ship Channel (HSC) and major tributaries. The sampling was performed on July 24, 1997. The TNRCC provided boats and sampling crew, and TAMU-TERL personnel collected and analyzed the samples using clean techniques.

SAMPLING DESIGN

The primary interest with trace metal data relates to wastewater discharge permits. Stations and metals were selected in concert with TNRCC staff with experience in Houston area permits. Also, the TNRCC was interested in obtaining quality data and agreed to participate in the sample collection. Figure 1 shows the locations of the selected sampling stations.

CLEAN PROCEDURES

Special precautions were taken to assure that sample collection, preservation, and storage would introduce no contamination. All equipment contacting the water sample (i.e., bottles, tubing sets and cartridge filters) were subjected to a rigorous acid cleaning procedures in accordance with EPA Method 1669 (EPA 1995), and double bagged to avoid contamination. Filter cartridges were pre-cleaned using hydrochloric acid, deionized water and double quartz distilled water, neutralized with ultrapure ammonium hydroxide and sealed in double plastic bags. In addition, separate glass bottles for mercury samples, carbon samples (i.e. total, particulate and dissolved) and total suspended solids (TSS) samples were used. The glass bottles were acid cleaned, combusted at 450°C for 8 hours and double bagged. Bottles and tubing sets are certified to be metal-free down to the method detection

limits (MDL) by taking equipment blanks. As required by EPA sampling method 1669, equipment and field QA samples were collected to confirm that the sampling was conducted consistently and cleanly (i.e. sampling was done without contamination). Detailed QA procedures and acceptance criteria are given in the project report (City of Houston, 1998).

SAMPLING PROCEDURES

As noted before, TAMU-TERL personnel worked on each of two TNRCC boats following clean procedures. The weighted end of the cleaned Teflon tubing was lowered to approximately 5 feet above the bottom, and the pump operated to flush the lines. After purging, the pump flow was continued while the tube was slowly raised to the surface, producing a depth-integrated sample. While the tube was raised, output from the peristaltic pump went to a fresh in-line Gelman 12175 filter cartridge, producing filtered samples that were immediately sealed, labeled, and placed on ice for transport to College Station.

In parallel with the metal sampling, the TNRCC field crew collected probe observations of dissolved oxygen, conductivity-salinity, temperature, and pH. These observations were made at 5-foot intervals.

Sampling was conducted over a broad geographic area from early in the morning until well after sunset. Late in the day, one the boats had engine problems. Retrieving this boat prevented one rather remote station from being sampled. Also, two stations were found to not be accessible by boat. With these minor limitations, the sampling effort was quite successful.

RESULTS

Table 1 presents the trace metal results along with the quality assurance samples. The data met all quality assurance criteria, with the Sampler and Field Blanks yielding expected results, and the field duplicates being very consistent with the original sample results. All the results are well below the lowest marine water quality criteria shown at the bottom of the table. The metal whose ambient concentration is closest to its criterion is copper.

During sampling the TNRCC crew collected probe parameters. Salinity ranged from about 20 ppt in the lower channel to approximately 8 ppt in the upper channel. Figure 2 plots some of the vertical DO profiles in the channel. Dissolved oxygen levels were typical for summer low flow conditions, with low values in the upper channel.

COMPARISON WITH OTHER TRACE METAL RESULTS

The samples reported here are not the first clean trace metal measurements on the HSC. Earlier results include: a 1993 joint TNRCC-Texas Department of Health project; a 1993-94 project by the City of Houston-EPA (City of Houston, 1995); Gulf Coast Waste Disposal Authority work in 1993-94; and a 1995 effort by TNRCC and the East Harris County Manufacturers Association (EHCMA). Table 2 compares results for samples collected in the San Jacinto River area, and Table 3 compares results for stations on the Ship Channel. The lowest marine criteria are shown at the top of each

table.

With the exception of the 1993 TNRCC-TDH study where the filters used appear to have leached some metals making the dissolved results unusable (they were frequently higher than the total metal concentrations), the results appear quite consistent. Silver and mercury were generally not detected even with the most sensitive methods. With the exception of the TNRCC-TDH values for Copper, Nickel and Zinc, all of the values appear quite consistent. In addition to the consistency among studies for samples from the same area, there appears to be very little difference between results obtained for the heavily industrialized Ship Channel stations and the much less developed stations on the San Jacinto River.

DISCUSSION

This study, together with previous high quality metal samplings, demonstrates that trace metal levels in the heavily industrialized and developed Houston Ship Channel are well below applicable marine criteria. However, previous experience has demonstrated the need to assure that rigorous measures are taken to assure quality results. When such measures are taken, it appears that levels are reasonably consistent among studies. Furthermore, it appears that levels are reasonably consistent between locations and largely independent of development and industrial activity. The values here are also similar to those found in other Texas estuaries by Benoit and Santschi (1991). This suggests that the levels of trace metals in estuarine waters may be controlled by geochemical processes and affected to only a small degree by anthropogenic activity.

ACKNOWLEDGEMENTS

Christine Kolbe, David Petrick and Charles Marshall of the TNRCC were instrumental in coordinating the work and collecting the samples.

Dr. Yu-Chun Su of PBS&J provided analytical support, and Dr. Lial Tischler of Tischler/Kocurek provided review and comments on the program and draft report.

REFERENCES

Benoit, G. and P.H. Santschi. 1991. Trace Metals in Texas Estuaries. Report prepared for the Texas Chemical Council. TAMU-Galveston.

City of Houston. 1995. Houston Ship Channel Toxicity Study Project Report. ENSR Doc. No 1591R001.01

City of Houston. 1998. Trace Metal Survey of the Houston Ship Channel. Report for the Texas Clean Rivers Program, H-GAC. EH&A with Omega Engineers.

Gulf Coast Waste Disposal Authority. 1994. Interim Final Report, Background Trace Metals for the Houston Ship Channel. Background Metals Study for Permit No. 01740.

US EPA. 1995. Method 1669. Sampling ambient water for trace metals for EPA water quality criteria levels. EPA 821-R-95034. Office of Water, Washington DC. 36 p.

_____. 1995. Method 1637: Determination of trace elements in ambient waters by chelation preconcentration with graphite furnace atomic absorption. EPA 821-R-95-030. Office of Water, Washington DC.

_____. 1995. Method 1640: Determination of trace elements in ambient waters by on-line chelation preconcentration and inductively coupled plasma-mass spectrometry. EPA 821-R-95-033. Office of Water, Washington DC.

_____. 1995. Method 1631: Mercury in water by oxidation, purge and trap and cold vapor atomic fluorescence spectrometry. EPA 821-R-95-027. Office of Water. Washington DC.