ATTACHMENT 9

FINAL REPORT

Title: COOLING WATER SYSTEM COPPER STUDY

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Technical Objective

The objective of the study is to examine the variability of aqueous free copper II ion ($Cu\ (II)_{(aq)}$) in the cooling water discharge of the South Bay Power Plant and to estimate the annual amount of copper (Cu) added to San Diego Bay by the plant's cooling water system. Details of the study's methods can be found in the SDG&E Revised Study Plan[1]. Factors examined for this report include:

1. The quantity and quality of data required to determine a statistically significant difference between the intake and discharge free copper concentrations.
2. The short-term variability of $Cu\ (II)_{(aq)}$ concentrations.
3. The influence of temperature, salinity, pH and time of day.
4. The tidal conditions that might induce mixing in the outflow channel.
5. The effect of rapid mixing of organic matter with the discharge in the channel.

The main potential sources of copper corrosion, in terms of area, are the plant's four condensers and eight heat exchangers. The plant's cooling water system utilizes up to 601 Mgal/D of San Diego Bay water. This water is used as once through, non-contact, cooling water to condense steam and to cool auxiliary equipment. Steam is condensed in four condensers (one per generating unit) and auxiliary cooling is accomplished through eight saltwater heat exchangers (six service water heat exchangers and two condensate heat exchangers). Water is drawn into individual cooling water intake structures for each unit, pumped through steam condensers and other heat exchangers and discharged back to San Diego Bay through four individual discharge pipes (one for each unit).

The anticipated parts per trillion increase in copper concentration of the cooling water from the system could occur as a result of corrosion of the system's components which are exposed to the cooling water. The significant components of the cooling water system, in terms of metal surface area exposed to the cooling water, are the condensers and heat exchangers, which present an estimated 392,000 ft^2 of exposed surface area.

The range of copper in the tubes is approximately 70-90%, except for the stainless steel condenser tubes in Unit No. 1 where the percent copper is a maximum of 0.75%. The corrosion rate for the stainless steel is considered nil. The copper released into the cooling water as a result of corrosion is released as Cu (II)$_{(aq)}$. This Cu (II)$_{(aq)}$ will complex with organic material in the bay water to form, and be in equilibrium with, other species of copper. The ambient equilibrium concentration of Cu (II)$_{(aq)}$, in San Diego Bay is approximately 1×10^{-14} molarity.

SPAWAR used a combination of Jalpaite-based Copper Ion Selective Electrode (Cu-ISE) and Graphite Furnace Atomic Absorption (GFAA) techniques to measure the concentration of copper in the cooling water intake and discharge channels. The GFAA was used as a confirmation method for the Cu-ISE. This unique technique outlined by Rivera-Duarte and Fengal[4] utilizes salt extraction with Cu concentration. When incorporated with trace metal clean techniques, this method can be used to determine nanomolar levels of Cu. Both of these methods are Research and Development (R&D) grade methods and were selected for this study because standard EPA approved analytical methods (i.e., methods found in 40 CFR 136) are not capable of quantifying small differences in copper concentrations at the micro-gram per liter level. The key SPAWAR project personnel are listed in Appendix I.

Study Design

This study was divided into two phases. The purpose of the first or pilot study phase was to determine what factors, environmental and physical, influence the copper activity and to develop measurement protocols that maximized the sensitivity of the instrumentation. Factors examined in this phase included the effects of pH, temperature, salinity, tidal currents, diurnal effects and instrument operational protocols and setup.

The purpose of the second or monitoring phase was to collect a sufficient amount of data, as indicated by the pilot study, to obtain an accurate estimate of the copper loading using the refined protocols and techniques developed in the pilot phase.

Pilot Study

Current Measurement

Currents were measured in the out-flow channel using a RD Instruments RD-SC Acoustic Doppler Current Profiler on December 17 through December 19, 1998[*]. The cooling water (CW) flow rates during the measurement period varied from a low of 314 Mgal/D to a high of 601 Mgal/D. Of the three days, the tides were at their greatest range on December 18. Figure 1 plots current velocity, vector direction and water level 3 feet from the bottom of the channel near the environmental sampling buoy on December 18. As expected the current velocity is at its maximum as ebb tide is approached and at a minimum as flood tide is approached. The current velocity never dropped below 12 cm/s and the velocity vector was always towards the channel exit.

Minimum Flow Calculations
Using the data gathered, the following calculations were used to estimate the minimum cooling water (CW) flow rate that will avoid mixing of the bay water and CW outflow. The following calculations are based on the data collected on December 18 and the following simplifying assumptions:

    1. At flood and ebb tide, only the CW pumps contribute to the channel flow velocity.

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[*] A full listing of the data is being retained by SPAWAR and is available upon request.

2. Flow is uniform across the channel.

3. Measured flow 3 feet above the bottom at mid channel is representative of the average channel flow rate.

4. There is a linear relationship to tide height and channel cross-sectional area.

Given:
- Measured current velocity at ebb tide +1.87ft. 0215 hours   18 cm/s
- Measured current velocity at mid tide   +4.25ft. 0522 hours   15 cm/s
- Measured current velocity at flood tide +6.64ft. 0830 hours   16 cm/s

CW flow rate 502.6×10^6 gal/D or 2.202×10^7 cm^3/s

Channel Cross-Sectional Area is estimated to be:

(flow vol. cm^3/s) / (flow vel. cm/s) = cross sectional area (cm^2)

At ebb tide $(2.202 \times 10^7$ cm^3/s) / (18 cm/s) = 1.22×10^6 cm^2

At peak tide $(2.202 \times 10^7$ cm^3/s) / (16 cm/s) = 1.38×10^6 cm^2

(ebb tide area+flood tide area)/2

At mid-tide $(1.22 \times 10^6$ cm^2 + 1.38×10^6 cm^2) /2 = 1.30×10^6 cm^2

Outflow at a mid tide of +4.25 ft. is calculated to be:

(vel. cm/s) (mid-tide area cm^2) = flow rate (cm^3/s)

(15 cm/s)(1.30×10^6 cm^2) = 19.5×10^6 cm^3/s

CW flow volume required for zero velocity outflow at a mid-tide of +4.25 ft. is calculated to be:

(CW flow vol.) - (mid-tide flow vol.)

$(2.202 \times 10^7$ cm^3/s) - $(19.5 \times 10^6$ cm^3/s) = 2.525×10^6 cm^3/s or 57.5×10^6 gal/D

Conclusion

Based on these calculations and simplifying assumptions, data should only be used when CW flow rates are at or above 100×10^6 gal/D. This is a conservative measure to ensure the discharge sample is not diluted by mixing with bay water. However, samples collected during an incoming tide (where CW rates are below 100×10^6 gal/D) can be used if results from a current meter demonstrate that mixing did not occur. During an incoming tide, with CW flow rates near 100×10^6 gal/D and without the use of a current meter, tidal variations should be no more than 7 feet and peak tides be no higher than +7 feet.

Pilot Study Measurements

Cu-ISE Background

The ion selective electrode used was an Orion 94-29[x] employing a jalpaite membrane calibrated against Cu-ethylenediamine and Cu-glycine buffers. This electrode measures free copper ion "activity". Activity (expressed as pCu) is a thermodynamic measurement of the Cu ion "pressure" of the system. Activity (which is unitless) is different from concentration in that it represents a steady-state concentration of Cu ion that is relatively invariant with time until the buffer capacity of the system is consumed or the buffering system itself is altered. Activity is analogous to a partial pressure (e.g., the partial pressure of oxygen). Any new discharge of copper, as Cu (II)$_{(aq)}$, into the channel is detectable with the electrode due to the kinetics of the buffering system. A significant portion is immediately bound by inorganic ligands in a 10000:1 ratio based on model calculations and confirmed by San Diego Bay water titrations[2,5]. The remaining newly released copper slowly complexes with organic ligands over a period of several hours which is much longer than the few minutes travel time from the condensers to the sample point in the outlet channel. The lifetime of the

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[x] Due to a typographical error, this electrode was incorrectly referred to as an Orion 90-24 in the Pilot Study.

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remaining newly released Cu (II)$_{(aq)}$ in seawater is dependent on the composition of the copper buffering system (organics, inorganics, colloids and particulates) and the level of mixing.

The response of the electrode to an increase in copper activity is typically 5-10 minutes. The response to a decrease in copper activity is typically 15-20 minutes. These response times must be taken into account during the real time measurements to minimize error.

Measurements

Sample sites were established in the intake channel adjacent to the NPDES intake monitoring buoy (i.e., mid-channel at the property line) and in the discharge channel adjacent to the NPDES Monitoring Station No. S2 (i.e., mid-channel at the property line). Continuous measurements of Cu (II)$_{(aq)}$, temperature, pH and salinity were taken. Cu (II)$_{(aq)}$ levels were measured using the techniques outlined by De Marco, Mackey and Zirino[3]. As seen in Figure 2, a computer controlled continuous flow system was constructed using a single sensor suite for measuring both the inlet and the outlet. Use of a single sensor was chosen to eliminate the inherent problems with inter-calibrating two sensors. The computer was programmed to alternate the sample flow every two hours. Because even trace amounts of chlorine will interfere with the Cu-ISE electrode, the sample flow was always switched, for two hours, to the inlet channel at the beginning of the plant's chlorine release cycle. In-line mesh strainers were cleaned on a daily basis. Grab samples were collected at the system sampling ports.

The measurement protocol for the pilot study was to monitor the inlet channel continuously for two hours, switch to the outlet channel and monitor it for two hours, then switch back to the inlet, repeating the cycle over three days. Each four-hour inlet-outlet data set would be used to statistically compare the Cu(II)$_{aq}$ levels.

A plot of all the continuous measurements over a three-day test period are shown in Figure 3[*]. The Cu (II)$_{(aq)}$ is plotted as pCu, which is -$\log_{10}$ of the Cu (II)$_{(aq)}$ activity. Note that, as pCu increases the concentration of Cu (II)$_{(aq)}$ decreases. The spikes seen in the pH and temperature curves are due to the switching of the pumps between the inlet and outlet. From Figure 3, it can be observed that the pCu levels for the inlet and outlet are not correlated with pH, temperature or salinity. There does appear to be a slight diurnal cycle in ambient levels of Cu (II)$_{(aq)}$ for the first two days of measurement that does not carry through to the third day. A more detailed view of the pCu is shown in Figure 4. From this figure, it can be observed that the concentration of Cu (II)$_{(aq)}$ is, as expected, higher in the outlet channel than the ambient levels in the inlet channel. Typical pCu levels in mid-to-outer San Diego Bay range between 10 and 13 pCu. With higher copper levels (lower pCu) found in basins with large copper sources (for example commercial basin) and lower levels (high pCu) near the entrance to the bay. Sharp peaks rising above 13 pCu are probably due to complexed-sulfide kinetics. Sulfides transported from the sediment into the water column can change the ambient equilibrium levels of Cu(II)$_{aq}$. This phenomenon is most noticeable in estuarine environments.

Averaging each sampling period and replotting the inlet-outlet data sets, as a bar graph, with two sigma (95.4% probability) error bars (Figure 5), it can be observed that for most data pairs the variability of the data, due to the lengthy measurement period, precludes definitively stating the pCu difference between the inlet and outlet. There are two inlet-outlet data sets that demonstrate a statistically significant difference, i.e. a difference greater than two sigma. Table 1 lists the value of these two data pairs. In this table the difference in parts per trillion was estimated using the model developed by Zirino and Yamato[5] and a Cu-ISE titration curve for the inlet channel. The model and titration curve are needed to account for copper chloride (CuCl) complexes and other rapidly complexing organics and ligands which reduce the Cu(II)$_{(aq)}$ levels before reaching the sensor.

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[*] A full listing of the data is being retained by SPAWAR and is available upon request.

Table 1. Values for the two inlet/outlet data pairs which exhibited a two sigma significant difference in pCu.

Outlet (pCu)	Inlet (pCu)	Outlet - Inlet Cu (II)$_{(aq)}$ (M)	Outlet - Inlet (model estimate) Cu (II)$_{(aq)}$ (μg/L)
13.1	13.6	5.4×10^{-14}	2.9×10^{-2}
12.8	13.1	7.9×10^{-14}	5.0×10^{-2}
	Average	6.7×10^{-14}	4.2×10^{-2}

Conclusion

From Figure 4 it is obvious that due to the variability of the pCu level that the chosen measurement period of two hours was too long. The sampling period should be reduced to account for the variability of the Cu (II)$_{(aq)}$ level.

During the pilot study, the gap between the reference electrode and the Cu-ISE sensor in the instrument manifold was maintained at 5mm. It was later found that by decreasing this gap to 1mm the sensitivity and response of the instrument was significantly improved. For the monitoring phase, the gap should be maintained at 1mm.

GFAA Copper Sampling

Samples for the GFAA copper measurements were collected, using clean techniques. Samples were collected at the Cu-ISE sampling ports during the Cu-ISE test period (3/8 - 3/11/99). Quality assurance followed the guidelines listed in Appendix II. Results of the quality assurance testing can be found in Appendix III. The GFAA sampling results are summarized in Table 2. From this table, it can be observed, in most cases, the inlet was higher in copper concentration than the outlet. This could be due to two factors. First, the time between inlet and outlet sampling varied from 35 minutes to 1 hour and 10 minutes. Based on the variability observed in the Cu-ISE data (Figure 4) this sample interval may have been too long. Second, it was observed that the turbidity of the samples varied. Since the samples were not filtered, the GFAA technique measured total copper. Thus, the differences seen between the intake and discharge sample results most likely were due to the amount of sediment copper contamination in the water column rather than the amount of copper added by the power plant.

Conclusions

During the monitoring phase, samples should be collected in a contemporaneous manner. Sampling time between the inlet and outlet should not exceed 15 minutes. Samples will be filtered on-site using acid washed metal free 0.45 micron filters to avoid collecting and measuring contributions of sediment copper contamination.

Table 2. GFAA Copper Measurements. The sample ID contains the sample port, time and date when the sample was collected.

Inlet			Outlet			Out-In
Sample ID	µg/L	Average µg/L	Sample ID	µg/L	Average µg/L	µg/L
IN 12:15 2-17	3.64		OU 11:55 2-17	4.05		0.41
IN 22:00 2-17	3.59	3.52	OU 22:20 2-17	3.98		0.46
IN 22:00 2-17	3.49					
IN 22:00 2-17	3.48					
IN 9:50 A 2-18	3.80	3.84	OU 10:20 A 2-18	3.82	3.88	0.04
IN 9:50 B 2-18	3.88		OU 10:20 B 2-18	3.93		
IN 21:40 2-18	3.73		OU 22:25 2-18	3.77		0.04
IN 9:50 3-9	3.57		OU 10:45 3-9	3.48		-0.09
IN 16:20 3-9	3.45		OU 15:30 3-9	4.48		1.03
IN 21:45 3-9	4.54		OU 22:15 3-9	4.13		-0.41
IN 5:50 3-10	4.38		OU 6:45 3-10	4.20		-0.18
IN 9:45 3-10	3.97		OU 10:30 3-10	3.91		-0.06
IN 16:25 3-10	3.87		OU 15:50 3-10	3.25		-0.62
IN 21:40 3-10	4.05		OU 22:15 3-10	3.79		-0.26
IN 5:45 3-11	4.20		OU 6:20 3-11	3.74		-0.45
IN 9:40 3-11	3.32		OU 10:20(1) 3-11	3.31	3.58	0.27
			OU 10:20(2) 3-11	4.08		
			OU 10:20(3) 3-11	3.36		
AVERAGE	3.81			3.85		0.01

Pilot Study Conclusions

The dynamics of the $Cu(II)_{aq}$ level combined with the two-hour measurement periods resulted in only two inlet-outlet data sets having statistically significant differences in $Cu(II)_{(aq)}$ concentrations. Reducing the sampling time to 30 minutes or less during the monitoring phase should minimize this effect. Additional Cu-ISE titrations of the inlet water will be conducted to further refine the correction factor between measured and actual $Cu(II)_{aq}$. These modifications to the sampling protocol should result in increased accuracy in determining the $Cu(II)_{(aq)}$ levels in the inlet and discharge channels.

The pilot GFAA results were disappointing but not unexpected. On site pre-filtering should correct errors caused by water column sediment contributions. It should be remembered that there is no direct comparison between the two methods because each is designed to measure two distinct components of the copper concentration. However, the trends of the two methods should track each other.

Pilot Study Summary

Sulfide complexation with $Cu(II)_{aq}$ can rapidly decrease the ambient level of $Cu(II)_{aq}$ in the water column. Sulfides transported from the sediment into the water column typically occurs in the estuarine environment. This would explain why these fluctuations have not been seen in other studies which utilized Cu-ISE measurements in the mid and outer bay. Accounting for this variability by decreasing the measurement time interval to 30 minutes without decreasing the number of sample measurements collected in an interval will result in improved data quality. In addition, monitoring for a three-day duration should be sufficient to observe any diurnal effects.

To ensure that mixing does not occur, the June sampling period should occur during the last week of the month when the tides will be within the previously determined tidal limits. During this period, CW flow rates should be maintained above 100×10^6 gal/D throughout the test period. Data collected at CW flow rates below this minimum will be excluded from the analysis.

GFAA samples will be pre-filtered and collected at the beginning, midpoint and end of the Cu-ISE sampling period. This should eliminate the effects of measuring Cu contaminated sediment in the water column. Blanks and field duplicates will be collected and measured according to the quality assurance plan.

Monitoring Study

Cu-ISE Copper Measurements

Utilizing the information obtained from the pilot study, continuous measurements of $Cu(II)_{(aq)}$, temperature and pH were taken. $Cu(II)_{(aq)}$ levels were measured using the techniques outlined by De Marco, Mackey and Zirino[3]. Data was recorded every two seconds for a period of three days. The pilot study computer controlled continuous flow system was used (Figure 2). Modifications to the system for the monitoring study included elimination of the salinity measurement, and reduction of the gap between the Cu-ISE and the reference sensor to 1mm. Salinity measurements were eliminated because they showed no correlation to pCu during the pilot study. The computer was programmed to alternate the sample flow every hour. This was altered from the original pilot study recommendation of 30 minutes because of the slow response of the Cu-ISE. When switching the Cu-ISE from the outlet to the inlet channel, 15 minutes was required to stabilize the reading. Using a 30 minute measurement period would not allow enough time to collect a statistically significant amount of data. Because even trace amounts of chlorine will interfere with the Cu-ISE electrode, the sample flow was always switched to the inlet channel at the beginning of the plant's chlorine release cycle. In-line mesh strainers were cleaned on a daily basis. GFAA grab samples were collected at the system sampling ports.

The measurement protocol was to monitor the inlet channel continuously for one hour, switch to the outlet channel and monitor it for one hour, then switch back to the inlet, repeating the cycle over three days. Due to the plant chlorination cycle, the inlet was typically monitored for a total of 2 to 3 hours while the system was waiting for the outlet to purge the chlorine from the cooling system before monitoring.

Cu-ISE Data Analysis

Data was collected during three sampling periods; May 3-5, June 29-July 1, and July 12-14, 1999. Technical difficulties with the sampling and measurement equipment in the May and July sampling

periods prevented collection of valid data samples[*]. In May, a power outage at the sampling site along with computer hardware failures prevented collecting enough data during the sampling period. In July, numerous sampling hose failures prevented collection of enough continuous data during the sampling period. New sampling lines were installed before starting the June sampling. The data obtained during the June sampling period was used for the copper discharge analysis. Based on the pilot study, this period of measurement is adequate to obtain statistically valid results for an accurate calculation of the amount of copper added to San Diego Bay by the power plant cooling water system.

Figure 6 is a series of plots of the Cu-ISE data over the three-day sampling period in June, 1999[*]. It can be observed that the general level of copper activity of both the inlet and outlet is dependent on the diurnal cycle, reaching a low in the early afternoon and peaking in the late morning. In contrast, the differences in activity between the inlet and outlet correspond to the tidal cycle. The largest differences occur during and just after the peak high tide. During low tides, the copper activity of the outlet is near or below the inlet activity. To explain this observation it must be remembered that the activity is dependent on the buffering complex and the degree of mixing.

The outlet channel, is a much more dynamic system than the inlet channel. At low tides the outlet channel becomes much narrower and shallower and the degree of water turbulence due to the cooling water discharge increases from nearly quiescent at high tides to vigorous mixing at low tides. This is in contrast to the smooth uniform flow exhibited by the inlet channel under all conditions. The turbulence of the outlet channel at low tide probably results in the transport of naturally occurring sulfides from the sediment into the water column. As observed in the pilot study, sulfides transported to the water column will lower the measured copper activity. Looking at high tide, when both channels have similar flow regimes, a higher activity in the outlet channel can be observed when compared to the inlet. Based on this observation, it was decided to calculate the copper load using data collected from the outlet channel that was within two hours of the peak high tide. In addition, due to the slow response time of the sensor only the last 45 minutes of the inlet data and outlet data was used for calculations in each inlet-outlet data set.

Copper Loading

In the June 29 – July 1, 1999 sampling period, four output-input data sets were within the two-hour windows of the three peak high tides. All four data sets meet the tidal/flow requirements recommended in the pilot study and all data sets were collected during periods of maximum cooling water flow rates (i.e., all cooling water pumps were on). Looking at Table 3, the average difference in copper concentration between the inlet and outlet channels during the four hour high tide windows and utilizing a two sigma error was 0.39 ±0.17 µg/L .

Table 3. Cu-ISE results during the peak high tide.

Inlet (pCu)	Outlet (pCu)	Outlet-Inlet (model estimate) $Cu(II)_{(aq)}$ (µg/L)
11.78 ±0.02	11.64 ±0.02	0.39 ±0.11
11.74 ±0.02	11.56 ±0.02	0.57 ±0.12
11.72 ±0.02	11.60 ±0.04	0.37 ±0.18
11.71 ±0.02	11.63 ±0.04	0.24 ±0.18
	Average	0.39 ±0.17

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[*] A full listing of the data is being retained by SPAWAR and is available upon request

The maximum cooling water flow rate for the power plant is 2.275×10^9 L/day. For an upper bound, assume that the maximum flow rate could be maintained for one year, then a total of 8.304×10^{11} liters (2.275×10^9 liters/day X 365days) of cooling water would flow through the power plant. If the average increase in copper concentration was 0.39 ± 0.17 µg/L and the plant discharged at its maximum cooling water flow rate for an entire year, then a total of $3.2 \times 10^2 \pm 1.4 \times 10^2$ kg (i.e., $7.1 \times 10^2 \pm 3.1 \times 10^2$ lbs.) of copper would be added to the bay annually.

GFAA Copper Measurements

The purpose of the GFAA sampling was to confirm the results obtained with the Cu-ISE. This approach was used because collecting and measuring enough GFAA samples to get a statistically significant result, using this complex experimental technique, would be impractical. Samples for the GFAA copper measurements were collected, using clean techniques. Samples were collected at the Cu-ISE sampling ports during the Cu-ISE test period (6/29 - 7/2/99). Quality assurance followed the guidelines listed in Appendix II. Results of the quality assurance testing can be found in Appendix III. The GFAA sampling results are summarized in Table 4. From this table, it can be observed, in most cases, the outlet was higher in copper concentration than the inlet. The average difference (0.28 ± 0.61 µg/L) between the outlet and the inlet agrees, within experimental error, with the data collected using the Cu-ISE (0.39 ± 0.17 µg/L). However, the two-sigma error (± 0.61 µg/L) of the GFAA's limited sample set precludes reaching a definite conclusion about the accuracy of that number (i.e., 0.28 µg/L). It is a strong indication, within the limits of the technique, that the Cu-ISE method is correlated with this more traditionally based (i.e., GFAA), but still experimental, method.

Table 4. GFAA Copper Measurements. The sample ID contains the sample port, time and date when the sample was collected.

Inlet				Outlet				Outlet-Inlet	
Sample ID	µg/L	Average µg/L	2σ	Sample ID	µg/L	Average µg/L	2σ	µg/L	2σ
IN6-29-99 9:20	3.20			OT6-29-99 9:35	3.44				
IN6-30-99 11:40	3.28			OT6-30-99 11:50	3.61				
IN7-1-99 9:40	2.99			OT7-1-99 10:15	3.37				
IN7-1-99 9:45	3.07			OT7-1-99 10:15	3.49				
IN7-1-99 9:45	2.97			OT7-1-99 10:19	3.18				
		3.01	0.01			3.35	0.31	0.34	0.32
IN7-2-99 13:40	3.00			OT7-2-99 15:59	3.22				
Totals		3.09	0.25			3.38	0.33	0.28	0.61

Propagation of Uncertainties in Statistical Calculations

From Tables 3 and 4 it can be observed that the uncertainty of the final value of copper discharged is larger than the uncertainty of the individual measurements. Almost all interesting scientific measurements involve two steps. One must first estimate the uncertainties in the quantities that are measured directly, and then find out how these uncertainties "propagate" through the calculations to produce an uncertainty in the final answer. There are several statistical rules that govern this propagation[y]. To arrive at the single copper discharge number in both Tables 3 and 4, the individual

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[y] For further reading on this subject the reader is referred to Taylor, R. J., 1982, "An Introduction to Error Analysis", Oxford University Press.

inlet data sets were added together then subtracted from the individually added outlet data sets. All of these operations (addition and subtraction) required the addition of the uncertainties resulting in a relatively larger uncertainty for the final copper number, when compared to the individual measurements. In addition, in Table 3, to convert from pCu to µg/L requires multiplication steps further increasing the uncertainty since the uncertainty must be multiplied by the same amount.

Conclusion

This study utilized two R&D grade methods to estimate the amount of copper added to San Diego Bay by the South Bay Power Plant cooling water system. These methods included an experimental GFAA technique and the Cu-ISE technique. The estimated increase in copper concentration from the cooling water intake to the cooling water discharge channel using the Cu-ISE method was 0.39 ± 0.17 µg/L and corresponds to an estimated maximum annual copper discharge of $7.1 \times 10^2 \pm 3.1 \times 10^2$ lbs. The estimated increase in copper concentration using the experimental GFAA method was 0.28 µg/L and appears to confirm the Cu-ISE estimate. This confirmation is significant because the researchers involved in the GFAA measurements and the Cu-ISE measurements purposely worked independently in the monitoring phase and were not aware of each others results until after they were completed. Both of these independent methods produced similar results with varying degrees of error.
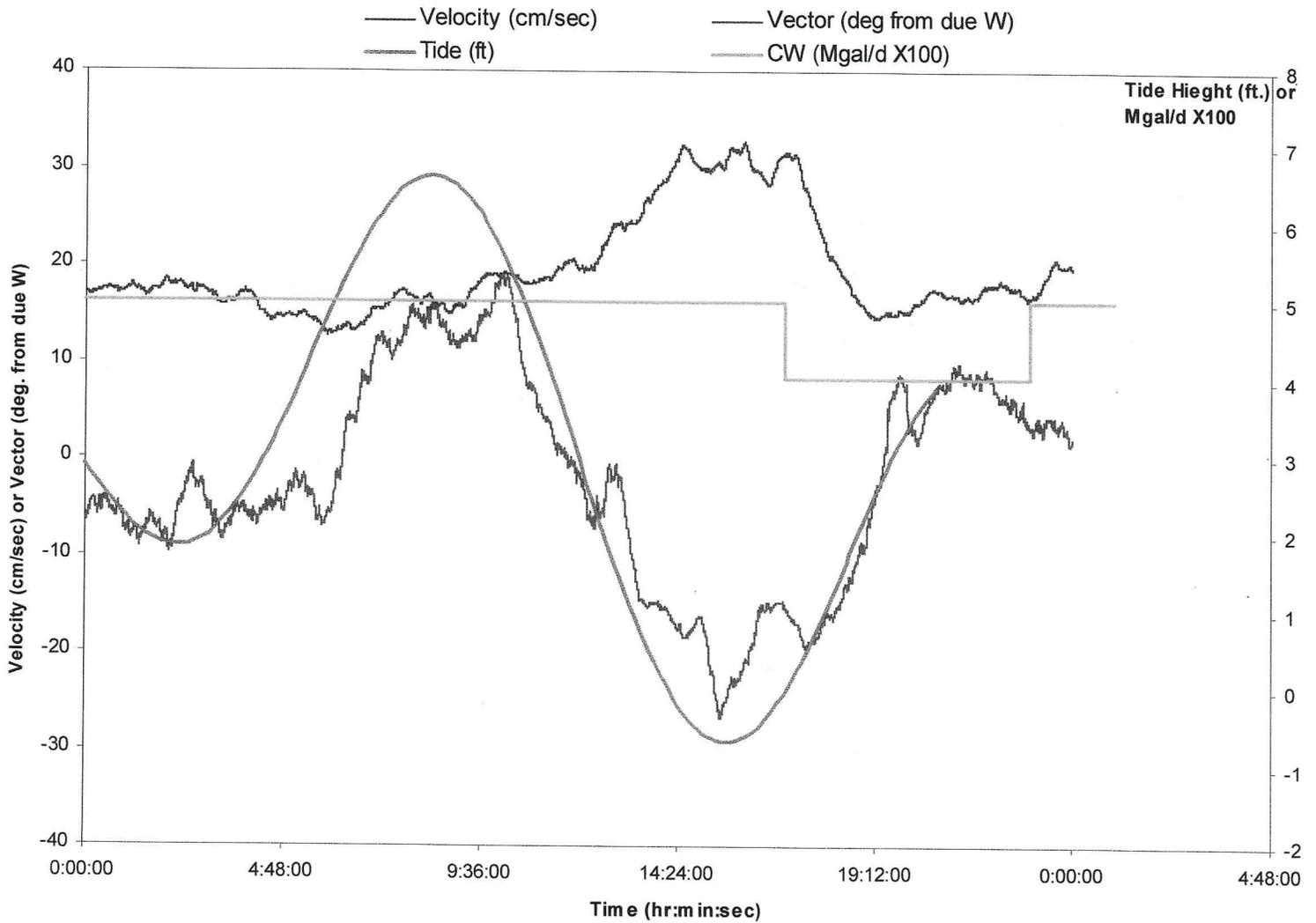
Outflow Channel
Dec 18, 1998

Figure 1. Tide measurements. The tide height was calculated using Micronautics tide prediction software. The current velocity and vector was measured by an acoustic doppler current profiler. Cooling water flow rates were obtained from power plant logs. It can be seen from this graph that the velocity vector was always towards the outlet of the channel and the velocity 64was never below 12 cm/sec.
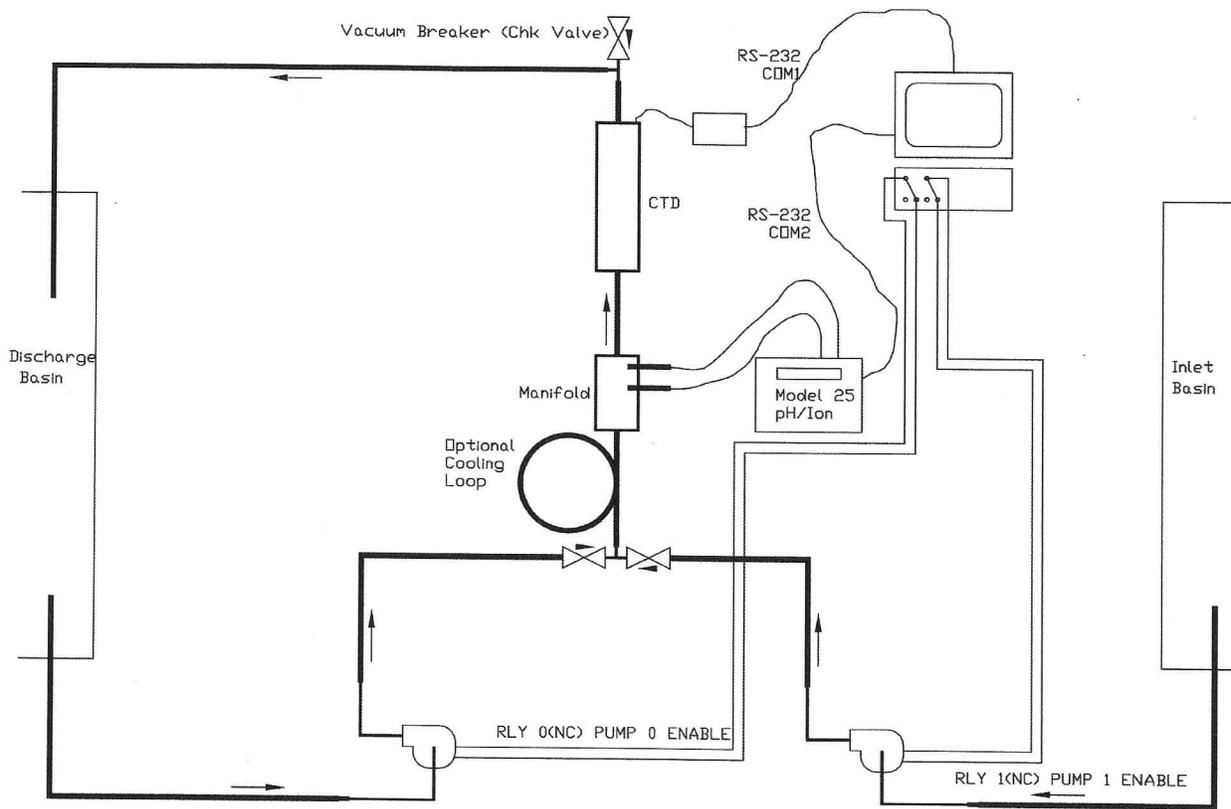
Figure 2. Schematic of the experimental setup. A single sensor suite was used to measure both the inlet and outlet channels. The pumps were computer controlled to switch at specified time intervals between the inlet and outlet.

Figure 3. pCu, temperature, pH, and Salinity measurements during the pilot study. For the pilot study the sensor suite was switched between the inlet and outlet on a two-hour schedule except during plant chlorination. The stray data points for temperature, salinity and pH are noise caused by the switch between the inlet and outlet pumps. It can be observed from this graph that at the resolutions measured, the pCu does not correlate with any of the other variables.
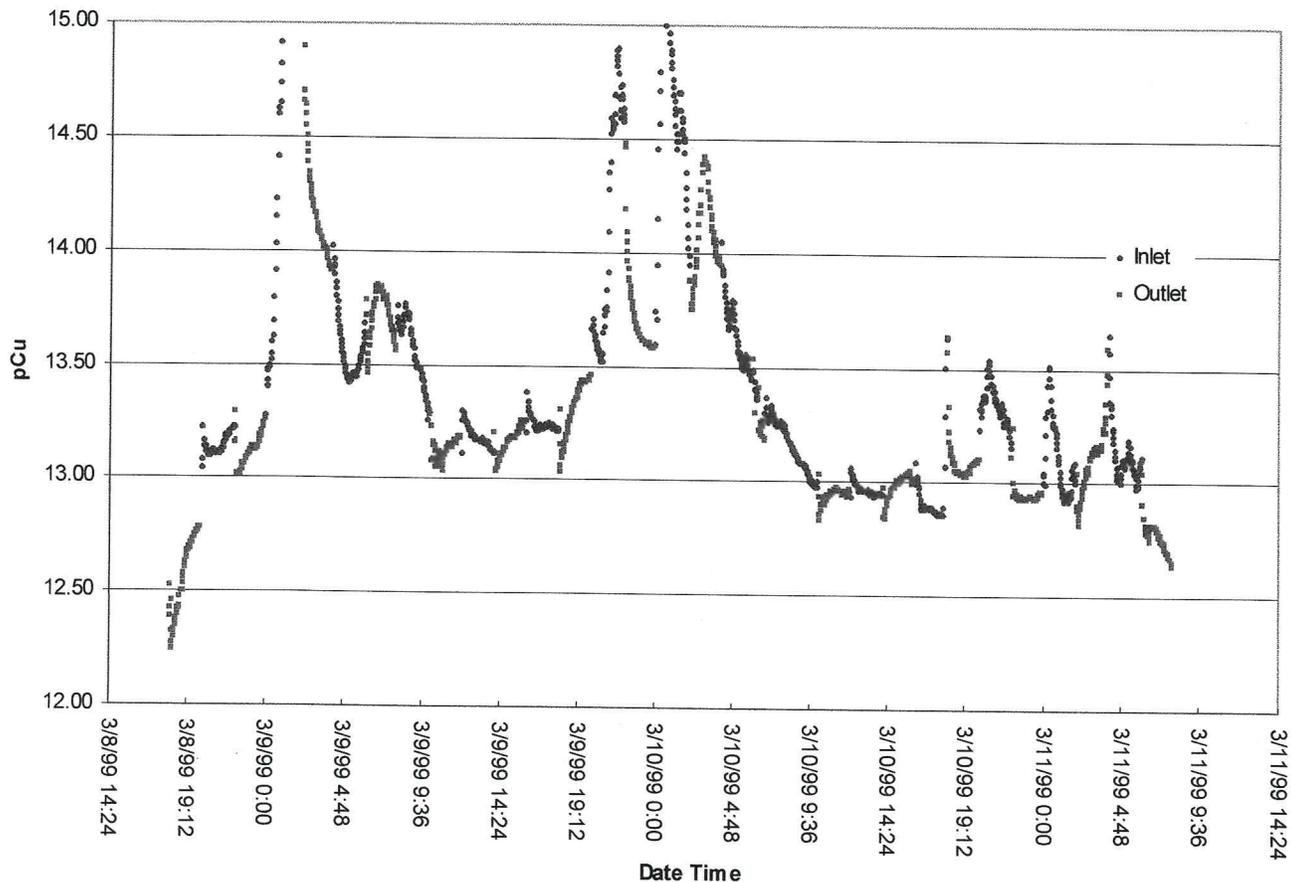
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Corrected pCu

Figure 4. An expanded plot of the pilot study pCu measurements corrected for temperature. pCu is the inverse log of the $Cu(II)_{aq}$ concentration higher values represent lower concentrations. The sharp peaks above 14.0 pCu indicate a sensor malfunction possibly due to contamination. This plot clearly demonstrates the variability of the $Cu(II)_{aq}$. concentration when compared to the selected two-hour sampling period. A sampling period of 30 minutes or less should reduce the sample measurement variability due to sampling protocol.
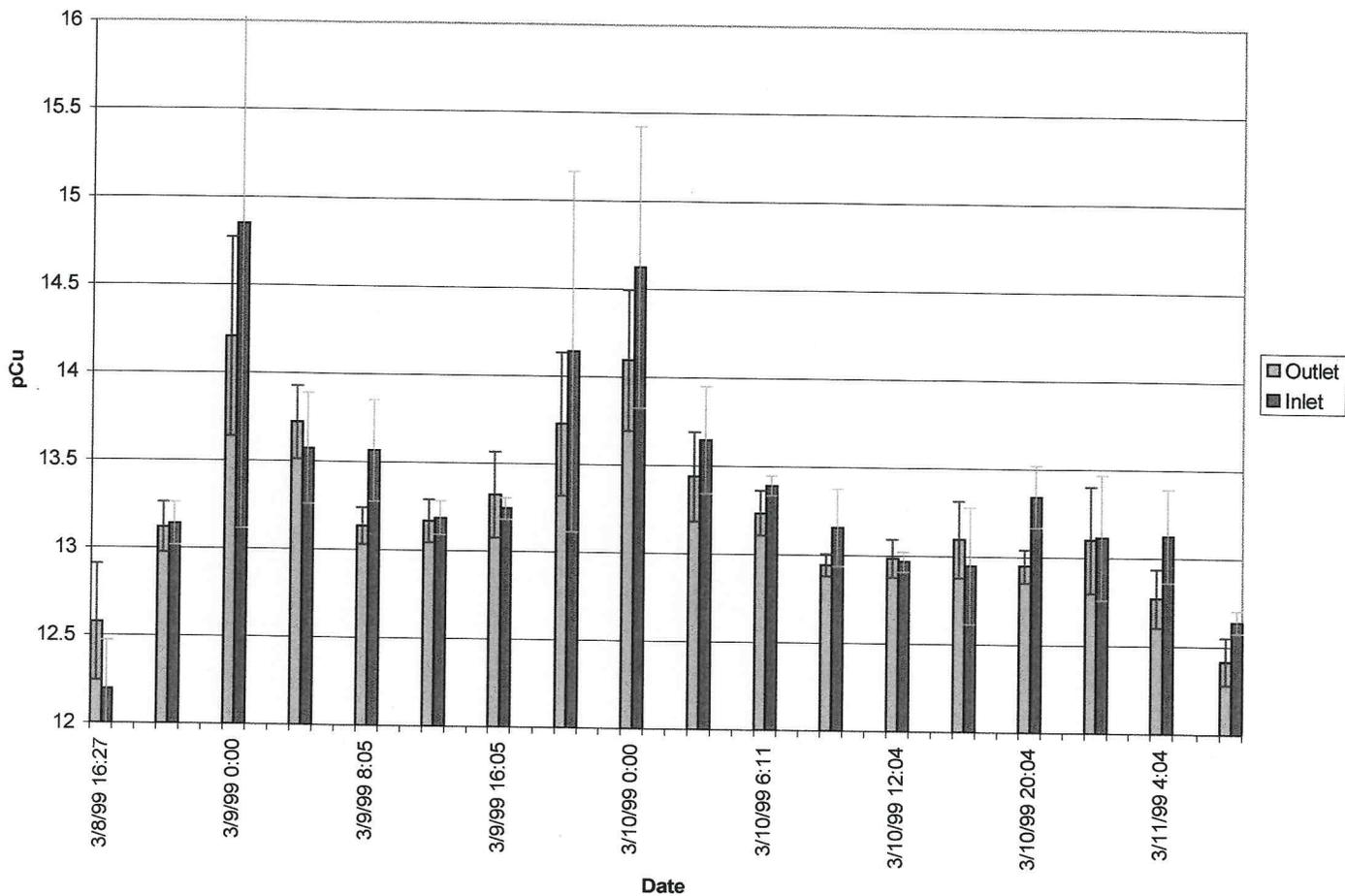
Figure 5. This bar graph plots the average value for each inlet/outlet pilot study data set in the pilot study along with plus or minus two sigma error bars. In all cases, except the first data set, the inlet was lower in $Cu(II)_{aq}$ concentration (higher pCu) than the outlet. Due to the lengthy sampling period compared to the pCu variability, only two data sets had differences greater than one standard deviation.
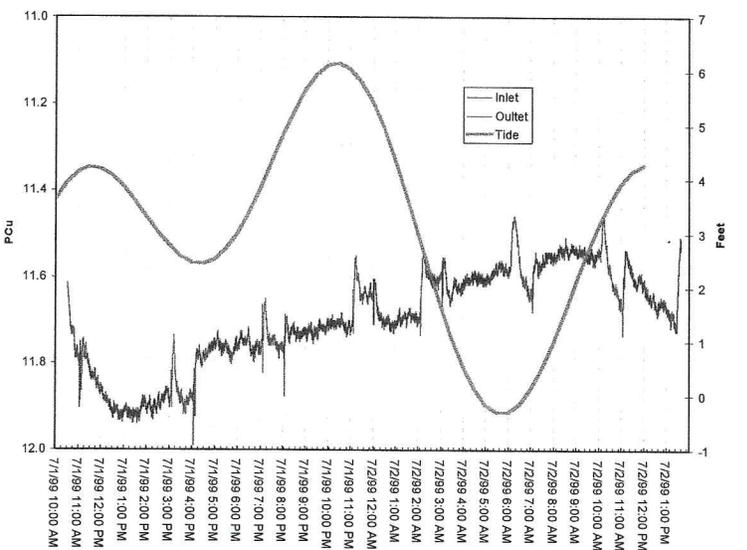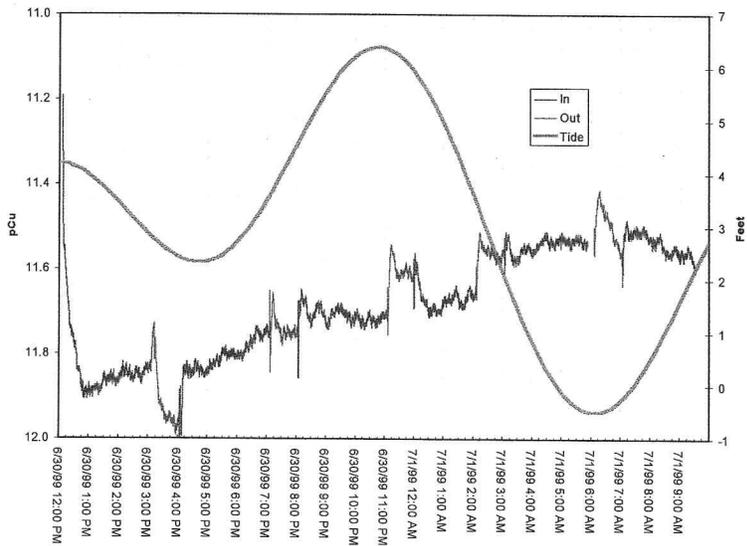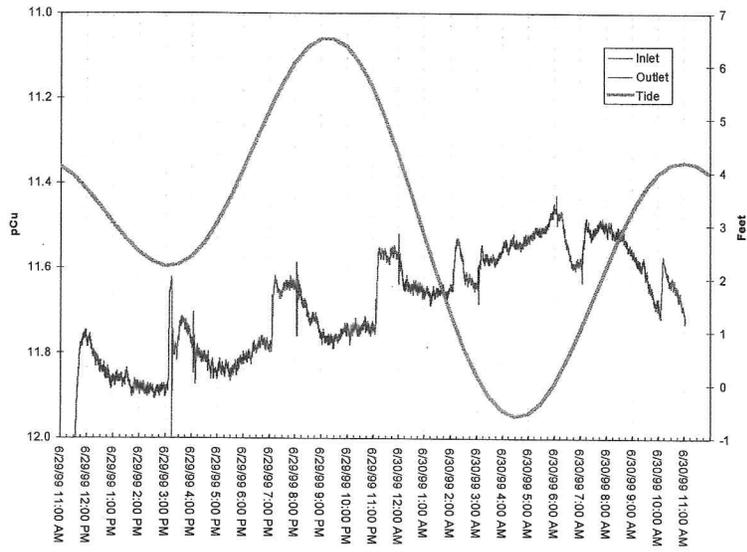
Figure 6. Cu-ISE and tide data from the monitoring study, June 29 - July 01. Each plot is approximately one 24hr. period.

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Key Project Personnel and Organization

Project Lead:
Mr. Mike Putnam
B.S., M.S. Biology, San Diego State University
M.S., Mechanical Engineering, San Diego State University

Mr. Putnam is head of the Environmental Chemistry Branch at SPAWARSYSCEN, San Diego. He is currently program manager on several projects involving the measurement of trace metals in industrial wastewater treatment plants, shipyard dry docks and shipboard effluents.

Senior Chemist:
Dr. Alberto Zirino
B.S., Chemistry, University of California, Los Angles
M.S., Physical Chemistry, San Diego State University
Ph.D., University of Washington, Seattle

Dr. Zirino is currently a Senior Research Scientist at SPAWARSYSCEN, San Diego. Additional appointments include Research Associate, Marine Research Division, Scripps Institution of Oceanography and Adjunct Professor, Department of Chemistry, San Diego State University. He has co-authored two books and published over 50 technical articles in the open literature. His current research grants, funded by the Office of Naval Research, involve studying alternative approaches to copper discharge regulations and modeling and prediction of the non-conservative behavior of copper in harbors and estuaries.

Chemist:
Dr. Ignacio Rivera-Duarte
B.S., Chemical Oceanography, Autonomous University of Baja California
M.S., Chemistry, University of the Pacific
Ph. D. Geochemistry, University of California, Santa Cruz

Dr. Rivera-Duarte is currently working at SPAWARSYSCEN, as a research scientist specializing in marine trace metal measurements. He is also an Adjunct Professor, Department of Physics, at San Diego State University. He has authored 16 journal articles in the area of wastewater pollution in the marine environment.

Lead Engineer:
Ms. Leslee Shumway
B.S., Electrical Engineering, University of California, San Diego
M.S., Environmental Engineering, University of Massachusetts, Amherst

Ms. Shumway is currently lead engineer for an air pollution particulate sampling and analysis study for the Navy Air Environmental Support Office. She has been project leader for test and evaluation on the Advanced Deployable Systems Program. Her duties included planning, coordination and implementation of tests conducted worldwide.

Appendix II

Quality Assurance

It is the responsibility of the quality assurance personnel to monitor the equipment, methods, and records throughout the demonstration and data analysis. They are to ensure the integrity of the data collected. The project lead will be assigned to quality assurance and will be on site during sample collection and measurement. He will review the data reduction and validation. The following protocols will be observed during the demonstration.

Sample Handling

Test samples will be collected, handled, and stored in pre-acid-washed containers. Each container will be clearly labeled with the specific source and treatment process of the sample, the name of the collector, and the date and time the sample was processed and analyzed. A chain of custody log will be kept for all samples. This log will accompany the samples during storage and movement, a current copy will also be kept on file. This log will note the date and time of sample movement, the location the sample is moved to, and the name of the person moving the sample. Samples analyzed off site will be tested within seven days of collection.

Samples will be collected, preserved and stored in accordance with EPA Method 1669: "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels" sections 8 and 9.

Equipment Blanks

Before using any sampling equipment at a given site, the laboratory will generate equipment blanks to demonstrate that the equipment is free from contamination. Equipment blanks will be used by the, test personnel, at the beginning of each field setup and at any time it is felt that the field equipment may have become contaminated. Reagent grade water or artificial seawater will be tested to verify non-contamination. Values of less than 10 times the level of interest (level of interest is estimated to be 0.1ppb), will be considered free of contamination.

Field Blanks

To demonstrate that sample equipment has not become contaminated during field sample processing one field blank will be generated for every ten samples that are collected at the site. If less than ten samples are collected, one sample will be collected for that session.

Calibration Blanks

Calibration blanks will be analyzed immediately after each calibration verification and provide a means of detecting contamination that arises from the analytical system.

Blank Decision Tree

If a contaminant is present in a blank but is not present in a sample, then there is little need for concern about the sample result.

If the sample contains the contaminant at levels of at least 10 times that in the blank, then the likely contribution to the sample result from the contaminant in the blank is at most 10%. Since the method in question is no more accurate than that level, the possible contamination is negligible, and the data

can be considered to be of acceptable quality.

If the sample contains the contaminant at levels of at least 5 times but less than 10 times the blank result, the numerical result in the sample should be considered an upper limit of the true concentration. Such data will be labeled and data users will be cautioned when using such data.

If the sample contains the contaminant at levels below five times the level in the blank, the sample data are suspect and will not be used.

Field Duplicates

To accesses the precision of the field sampling and analytical processes, one field duplicate sample will be collected for every ten samples. If less than ten samples are collected, one field duplicate will be collected for that session. The field duplicate provides an indication of the overall precision associated with the entire data gathering effort, including sample collection, preservation, transportation, storage, and analysis procedures.

Method Detection Limit and Quantitation Level

To establish the ability to detect the copper the analyst shall determine the MDL according to the procedure in 40 CFR 136, Appendix B using the graphite furnace, reagents, and standards that will be used in measuring the field samples. By modifying the sample preparation and preconcentration techniques, the laboratory will produce an MDL that is not more than one-third the expected concentration difference of 0.1ppb between the intake and outflow channels. The quantitation level will be calculated by multiplying the laboratory-determined MDL by 10.

Linear Calibration Range

The upper limit of the linear calibration range will be established by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper limit should be an observed signal no more than 10% below the level extrapolated from the lower standards.

Method Accuracy, Recovery and Precision

A standard reference material (SRM) will be used to calculate the accuracy, precision and recovery of the method. Either one of the two (CASS-2 and CASS-3) Nearshore Seawater Reference Materials for Trace Metals certified by the National Research Council of Canada, will be analyzed in triplicate for each sampling period. The results of these analyzes will be used to calculate the accuracy, recovery and precision of the method. And these values should be within 15% of the certified values (CASS-2 0.675 ± 0.039 ppb Cu; CASS-3 0.517 ± 0.062 ppb Cu).

Data

The field data will be stored on the hard disk of the instrument. When data collection is complete, the data will be backed up on floppy disk. Each run stored on disk will be identified, in the comment section of the data record, with the sample number, the origin of the source, and the date and time the sample was collected. The date and time the sample was analyzed will be recorded in the data record file name. All data collected will be managed in accordance with EPA document EPA 821-B-96-002 "Guidance on the Documentation and Evaluation of Trace Metals Data Collection".

Other

QA/QC methodology not explicitly described in the preceding text will follow EPA "Guidance on the Documentation and Evaluation of Trace Metals Data Collected for the Clean Water Act Compliance Monitoring (EPA 821-B-96-002) and Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels". Method specific QA/QC will follow Rivera-Duarte and A.R. Flegal, Anal. Chim. Acta., 328 (1996) 13.