LONG ISLAND SOUND STUDY
EPA ASSISTANCE AWARD FINAL REPORT

1. **Submission Date of Final Report to LISS: February 28, 2007**

2. **EPA Grant Number and Project Title: LI-97296600-0;** Temporal & Spatial Changes in Copper Speciation and Toxic Metal Concentrations in Long Island Sound: Effects of Changes in Water Temperature and Dissolved Oxygen Levels

3. **Grantee Organization and Contact Name:** Marine Sciences Research Center, Stony Brook University; Dr. Sergio Sañudo-Wilhelmy

4. **Public Summary:**

Since the Clean Water Act was passed in the 1970s, billions of dollars have been spent to decrease the input toxic contaminants to coastal waters. In spite of this enormous effort, recent research has shown that levels of toxic trace metals in the coastal ocean have not always decreased. In major urban estuaries such as the Long Island Sound (LIS), the effect of these toxic metals may have significant impacts on the ecological and economic health of the system. For example, preliminary evidence suggests that diseased lobster in the LIS may be suffering to some degree from copper toxicity. Because of this, it is absolutely imperative that research efforts be directed toward understanding of how biogeochemical cycles are regulating toxic metal presence and mobility in coastal waters. Furthermore, it is well established that simply knowing the total amount of dissolved metals in the water is not sufficient to understand how toxic the metal may be to organisms. Instead, it is necessary to separate the individual total dissolved metal pools into different forms, or “species”. Because of the evidence of its toxicity in LIS lobsters, we focused our study on dissolved copper. During two research cruises in spring and summer 2005, we measured the levels of total dissolved copper throughout surface and bottom water of the Sound. We also isolated the labile, presumably toxic, copper fraction from the total dissolved pool. In addition, we examined the non-toxic copper species which are complexed with dissolved organic matter.

Our results showed significant amounts of labile copper throughout the LIS, with the highest levels in the western Sound near New York City. This was the same pattern we found for total dissolved copper. During the spring season, “toxic” copper was higher in surface waters and was probably delivered during these high-flow conditions by river runoff and sewage. In both seasons, there was evidence that microscopic algae in the surface waters were producing organic compounds to complex the dissolved copper, thereby making it less toxic. In the summer, bottom waters of the western LIS were characterized by poor water quality, very warm and depleted of oxygen. In these deep waters, “toxic” copper was greatly elevated relative to the spring season and other places within the LIS. The data showed that poor water quality resulted in increased levels of toxic copper species. The greatest influencing factor was temperature; as water temperature reached a threshold greater than about 20°C, “toxic” (labile) copper concentrations increased very rapidly. Analyses of other chemical constituents suggested that the source of this “toxic” copper was the sediments.

Most toxic metals tend to attach strongly to the surfaces of particles, which then sink and are accumulated in the sediments. Because these sediments accumulate slowly, a century or more of metal pollution in coastal waters can be preserved in very shallow sediment deposits. Decreasing oxygen and increasing temperature can release these metals back to the water column. We believe our data indicate

that these metals are released in a potentially toxic form, making this process very important for biological organisms. In the Long Island Sound, bottom water temperatures are increasing each year; this means that the influence of toxic trace metals in the Sound will probably become more important in the future. There is an urgent need for future research to examine this phenomenon in greater detail; if we can understand how it happens, we may have hope of mitigating it in the future. Certainly, for industries such as the lobster fishery in the LIS, the socioeconomic consequences of such research are enormous.

5. Project Period: 06/01/2004-11/30/2006

6. Project Description:

This project sought to accomplish two goals: first, to establish temporal and spatial variations in the levels of dissolved Cu in the water column (surface, intermediate and bottom water) of the LIS, and second, to establish temporal and spatial variations in the chemical speciation (organic vs. labile, inorganic) of dissolved copper in those same samples. Cu was particularly chosen because the high susceptibility of crustaceans to Cu toxicity suggests that it may have had a role in the recent catastrophic lobster die-offs in the Long Island Sound. The objective of this study was to examine the geochemical cycling of the chemical species of Cu both spatially and seasonally, to better understand the possible role that its toxicity may have on the LIS ecosystem.

7. Activities & Accomplishments:

Sampling Cruises

Two cruises were conducted during 2005 to examine differences in metal speciation associated with spring (April 26-29) and summer (September 6-9) conditions. The sampling stations were distributed throughout the Sound, with higher spatial resolution in the East River and western LIS (Fig. 1 and Table 1).

Sample Collection and Analysis

Water samples were collected at each station from approximately one meter below the water surface (hereafter termed "surface") and one meter above the sediment surface (hereafter, "bottom"). A Teflon air-operated diaphragm pump (Warren Rupp) was used to pump water on board through acid-cleaned Teflon tubing, which was extended away from the ship on a boom. Water for trace metal and nutrient analysis was filtered through a 0.22 μm acid-washed polypropylene capsule filter directly into acid-washed LDPE bottles. All samples were handled under the rigorous protocols necessary for trace metal determination (1-3).

Samples for total dissolved metals analysis were acidified with ultrapure HNO_3 to pH<1 and stored for at least one month. Metals (Ag and Cu) were then preconcentrated following the APDC/DDDC organic extraction technique described by Bruland et al. (4). Total dissolved metals and metal speciation extracts were quantified by ICPMS using standard addition techniques. Dissolved PO_4 was determined by standard spectrophotometric methods (5). Size-fractionated chlorophyll *a* was determined by the non-acidification fluorometric method according to Welshmeyer (6).

Speciation Protocol

A detailed explanation of the speciation technique is excluded here. A brief summary of the separation methods follows: kinetically-labile Cu was operationally defined using extraction at natural pH onto Chelex-100 (mesh size 100-200) at a flow rate optimized to maintain short contact time between the sample and resin. At the flow rate (10 ± 1.4 mL min^{-1}) and resin volume employed (1 mL), the extractable metal species have been shown to be the bioavailable/toxic forms (7). Furthermore, the chemical speciation results using this Chelex approach are comparable to those obtained by voltammetric techniques (8, 9), and can provide useful information on the physical and kinetic partitioning of dissolved Cu (10). To determine the non-labile C-18 extractable organic fraction, a column containing C-18 Bondesil resin was placed in series after the Chelex-100 column (11). Thus, our "non-labile organic" (NLO) fraction represents the strongly-bound portion of the organic pool (12).

8. **Modeling:** [No computer modeling was used in this project.]

9. **Summary of Findings:**

(All data discussed below can be found tabulated in Table 2. Trace metal blanks and instrumental detection limits are listed in Table 3.)

During the spring cruise, water temperatures ranged from 5-11°C, with highest temperatures in the western Sound. The water column of the LIS was well oxygenated at that time, with concentrations ranging between 0.44-0.69 mM. During the summer cruise, water temperatures ranged between 19-24.5°C. Dissolved oxygen was generally ≤ 0.44 mM, with nearly hypoxic levels (< 0.19 mM) in bottom waters of the western and central basins of the Sound.

Total Dissolved Cu

Total dissolved Cu concentrations in both seasons followed a similar spatial pattern to that observed by Buck et al. (2), with highest levels approaching 28.6 nM in the western LIS, and declining eastward to less than 5 nM (Fig. 2a). The relatively low values measured in the easternmost stations were still about twice the ~3 nM levels reported for surface waters of the North Atlantic near LIS (13). Dissolved Cu levels in surface waters of the LIS were lower in 2005 (average ± s.d.; April: 15.9 ± 4.3 nM, September: 12.2 ± 3.5 nM) than were reported for 1999 (June-July: 20.8 ± 2.6 nM; Ref. 3) or 2000-2001 (April 2001: 22.2 ± 7.8 nM; July 2000: 22.4 ± 7.1 nM; Ref. 2). Dissolved Cu decreased slightly in the western basin under low flow summer conditions (14.3 ± 1.8 nM) as compared to high flow conditions (18.5 ± 3.7 nM), consistent with trends observed previously (2), and indicating that river discharge and wastewater effluent were important sources of Cu during these cruises. Although mean bottom water concentrations tended to be lower than those at the surface (spring surface: 15.9 ± 4.3 nM, spring bottom: 15.1 ± 3.7 nM; summer surface: 12.2 ± 3.5 nM, summer bottom: 11.4 ± 3.6 nM), the trend was not consistent for all stations (Fig. 2a).

Total dissolved Cu concentrations exhibited an almost linear distribution over the salinity range (~20-30) covered during our cruises (Fig. 2b), suggesting that conservative mixing between eastern and western LIS waters could influence water column Cu levels. The zero-salinity intercept (65 nM) obtained in the linear regression of all the dissolved Cu and salinity data is within the dissolved Cu range reported for Connecticut Rivers and NYC/Connecticut municipal wastewater effluent (40-270 nM; Refs. 2, 14, 15). Therefore, the cycling of Cu within the LIS seems to be influenced by both anthropogenic sources and advective mixing.

Dissolved Cu Speciation

C-18 extractable Cu

Average levels of non-labile organic (NLO) Cu were 5.8 ± 2.8 nM during the Spring cruise and 4.0 ± 1.4 nM during summer for the whole LIS (Table 2). This fraction represented 23-70% of the total dissolved pool during the spring cruise, and 21-51% during the summer cruise. Correlation of NLO Cu and the <2.0 μm chlorophyll *a* fraction suggests that small phytoplankton may have influenced the Cu speciation in surface waters during both seasons (Fig. 3). Indeed, the <2.0 μm phytoplankton community in the LIS primarily comprises the picocyanobacterium *Synechococcus* (C. Gobler, Marine Sciences Research Center – Stony Brook University, pers. comm.), which has been shown to produce organic chelators that strongly complex dissolved Cu (Ref. 16, and references therein). Furthermore, although the biomass of this phytoplankton size class does not vary between seasons, the slope of the NLO Cu – Chl *a* relationship in spring is double that in summer (Fig. 3). This suggests that during spring high flow conditions, when elevated levels of labile Cu are present in surface waters (see below), the picocyanobacterial community is actively producing more of these ligands to reduce the toxicity of Cu in the water column. In addition, the relationship has the same y-intercept for both seasons (Fig. 3), indicating a temporally constant buffering capacity of about 3 nM for labile Cu in surface water of the LIS.

Chelex-labile Cu - Spring season

Chelex-labile dissolved Cu levels in spring ranged between 1.3 and 6.4 nM, comprising about 10-30% of the total dissolved pool (Table 2). Labile Cu concentrations during spring were highest in surface waters of the western and central LIS (average ± s.d.; 4.6 ± 1.5 nM vs. 2.9 ± 0.9 nM in the eastern LIS), which likely resulted from input during high flow conditions from rivers and wastewater effluent. The wastewater source of labile Cu is supported by the significant correlation with sewage tracers (Ag and PO_4; Ref. 17) observed in surface waters during the spring cruise (Ag: $r^2=0.53$, $P<0.01$; PO_4: $r^2=0.39$, $P<0.05$; Figs. 4a and 4b). The lack of correlation between labile Cu and Ag ($r^2=0.02$; Fig. 4c) and PO_4 ($r^2=0.004$; Fig. 4d) in bottom waters of the LIS strongly suggests that the source of labile Cu to surface waters of the Sound was wastewater effluent.

Chelex-labile Cu - Summer season

In contrast to the spring results, labile Cu measured in the summer ranged from 0.33 to 7.7 nM, with highest levels measured in bottom waters of the western Sound (Table 2). While these levels were similar to those observed in surface waters during the spring cruise, labile Cu in summer represented as much as 45% of the total dissolved Cu in the western Sound, more than double that observed in the same location during spring. Labile Cu levels in surface waters during summer (range: 0.33-4.4 nM) were lower than the concentrations measured during high-flow conditions in spring (range: 2-6.4 nM), further confirming an external wastewater source in the spring. However, concentrations of labile Cu in bottom waters nearly doubled in summer (0.22-7.7 nM) as compared to spring (1.3-4.9 nM). The greatest increase in labile Cu was observed in the westernmost station (East River, Station 18), where spring levels were only 1.5 nM compared to 7.74 nM in summer.

During summer, labile Cu concentrations in bottom waters were highly correlated with both Ag ($r^2=0.83$, $P<0.001$; Fig. 5a) and PO_4 ($r^2=0.93$, $P<0.001$; Fig. 5b). These correlations cannot be ascribed to recent sewage sources as was argued for the spring cruise because such effluent would primarily affect surface waters, where much weaker correlations were observed with both Ag ($r^2=0.13$; Fig. 6a) and PO_4 ($r^2=0.32$; Fig. 6b) during this cruise. Instead, it is probable that all of these constituents are being delivered in a similar manner to bottom waters of the LIS by sedimentary diagenesis, as described below.

Evidence of labile Cu input from diagenetic remobilization

Chelex-labile dissolved Mn reached levels as high as 2.4 μM in bottom waters of the western LIS (Table 2). Labile Mn was observed in both surface and bottom waters, but was consistently higher in the latter. Elevated concentrations of labile Mn in bottom waters of the western LIS during the summer were more than 3 times the highest levels measured in spring (0.7 μM), and were two orders of magnitude greater than the levels seen in the fully oxic eastern LIS during summer (0.02 μM) (Table 2). This suggests that the active diagenetic cycling of Mn-oxides in surficial sediments and the resultant benthic flux of reduced Mn out of the sediments could be responsible for the high Mn levels measured bottom waters of the LIS. These results are consistent with the established pattern of benthic Mn flux within the LIS, which tracks seasonal variations in water quality parameters and primary productivity: Mn-oxides accumulate in the sediments during winter, undergo punctuated loss in response to high organic carbon flux after the spring phytoplankton bloom, followed by prolonged loss during warm hypoxic summer months and a transition to storage again in the fall (18).

The significant relationship (r^2=0.68, $P<0.001$) between labile Cu and labile Mn in bottom waters of western LIS during summer (Fig. 7) provides strong evidence that labile Cu was being remobilized during the diagenetic reduction of sedimentary Mn-oxides, as observed for total dissolved Cu elsewhere (19). In addition, our argument for a benthic source is further supported by correlation of labile Cu with other dissolved constituents of diagenetic source (e.g., PO_4 and Ag). Both PO_4 and Ag are closely tied to the cycling of metal oxides in surficial sediments (20, 21), and their strong correlation with labile Cu (discussed below, Figs. 5a and 5b) indicates that most of the labile Cu observed in bottom waters of the LIS was derived from benthic remobilization.

Effect of temperature and dissolved oxygen on labile Cu concentrations

The correlation observed between labile Cu and tracers of benthic remobilization suggests that some of the environmental variables controlling diagenetic processes such as water temperature and dissolved oxygen may also influence the levels of labile Cu within the LIS. Consistent with that hypothesis, under summer conditions when benthic remobilization is more significant (18), labile Cu levels in bottom waters of the LIS were correlated with water temperature and dissolved oxygen levels (Figs. 8a and 8b). A multiple regression analysis (of log labile Cu vs. temperature and oxygen) indicates that oxygen and temperature together explain 97% of the labile Cu variation in bottom waters of the LIS.

The influence of temperature is much stronger (alone explaining 82% of the variability) than that of oxygen (59%). This is of paramount concern, as bottom water temperatures are rising steadily in the LIS (22). In fact, temperatures are approaching the 21°C threshold at which benthic fluxes within the LIS become exponential (23, 24). Similarly, concentrations of labile Cu in bottom waters of the LIS also increased exponentially at water temperature >21°C (Fig. 6b). Therefore, future increases in water temperature due to global warming could result in increased labile Cu input to the water column from sediments. Considering that Cu from a benthic source appears to be kinetically labile indicates that this input will be of the greatest ecological relevance.

Oxygen levels also explained a significant portion of the variability observed in labile Cu concentrations in bottom waters, suggesting that this variable strongly influenced Cu speciation (Fig. 8a). The high levels of labile Cu observed under low oxygen levels in LIS bottom waters is consistent with the fact that under such conditions, decreased oxygen penetration into the sediments maximizes the benthic Mn flux (18). Previous studies have shown that benthic remobilization of total dissolved Cu increases under oxic conditions by increasing the solubility of Cu precipitates (25, 26). However, our results showed that when dissolved oxygen was high in bottom waters, the lowest levels of labile Cu were observed (Fig. 8a). Therefore, increasing oxygen levels by control of eutrophication in the LIS could potentially have the beneficial effect of reducing the amount of labile Cu in the water column.

By applying an operationally-defined fractionation method, we have been able to separate labile and organic Cu species from the total dissolved pool. Although total dissolved Cu levels in the LIS during spring and summer 2005 did not vary greatly, the labile fraction of this element showed clear evidence of active seasonal cycling. The data suggest that labile, potentially bioavailable Cu has a diagenetic source, and is strongly dependent on increasing temperature and decreasing levels of dissolved oxygen.

The results observed in this study demonstrate that the measurement of total dissolved trace metals as is currently performed on a regular basis may not be sufficient to observe changes occurring within the dissolved pool. It is critical that future studies begin to better characterize the distribution of chemical species within this pool. It is also immediately apparent that metal cycling in coastal ecosystems may already be responding to global phenomena such as temperature rise in subtle yet profound ways. The observations reported here demand that a more substantial effort be applied to characterizing the biogeochemical cycling of trace metals in coastal ecosystems, in order in order to be aware of the effects of global change.

References

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FIGURES and TABLES

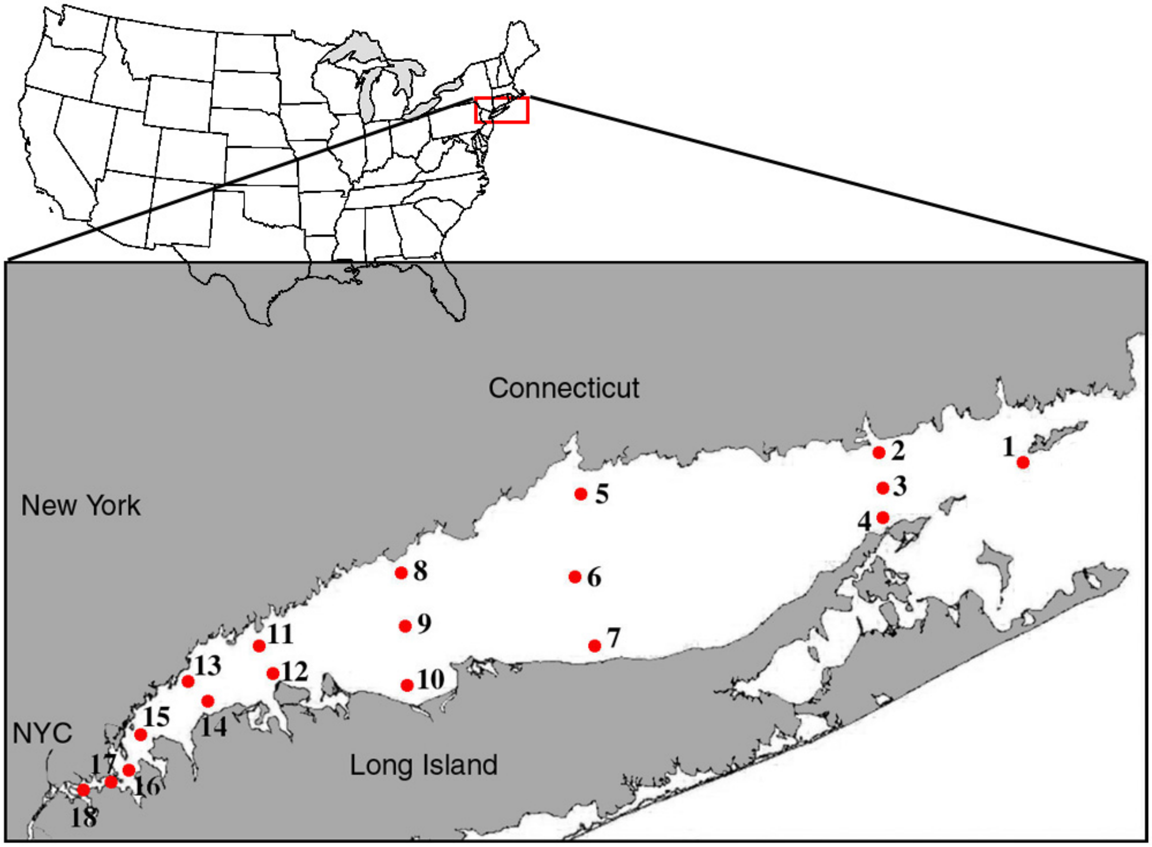

FIGURE 1. Map of Long Island Sound with locations of sampling sites indicated.

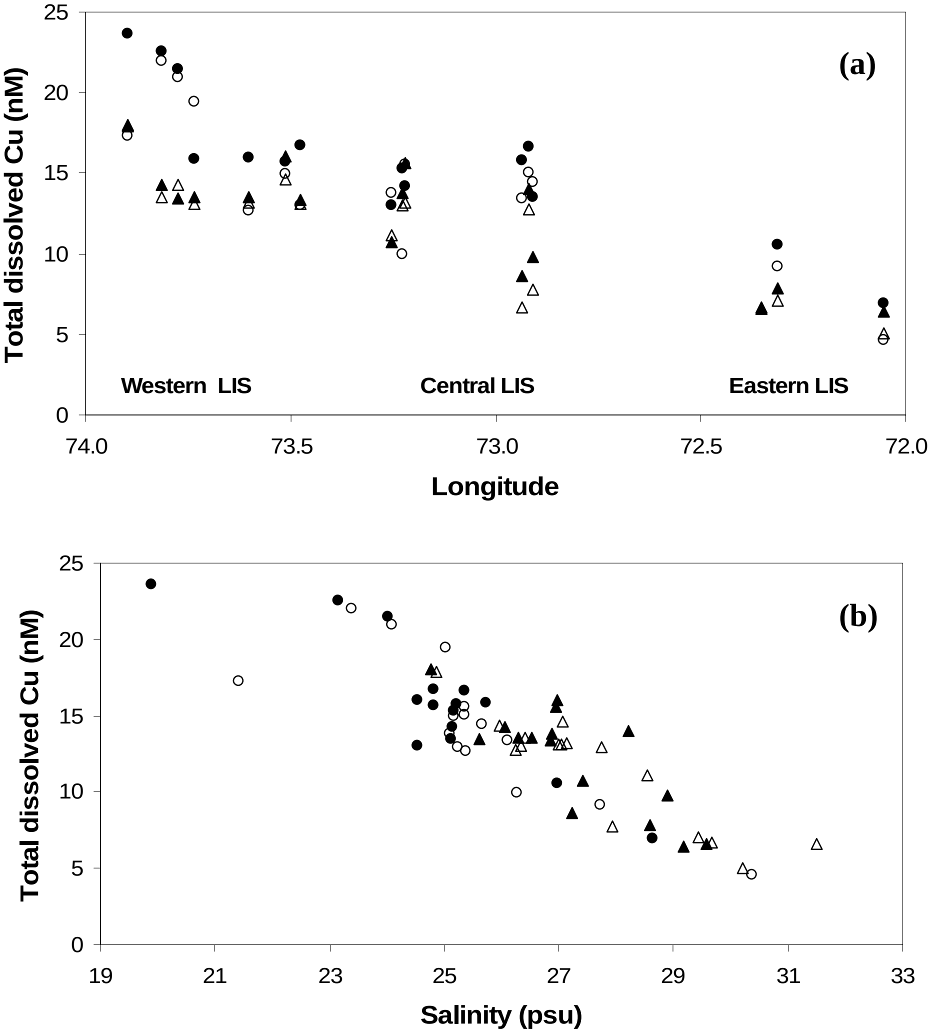

FIGURE 2. Total dissolved Cu. Circles represent the spring cruise and triangles represent the summer cruise. Filled and hollow symbols denote surface and deep samples, respectively. This convention will be followed in all graphs. (a) Geographical distribution of dissolved Cu in LIS. Westernmost stations are in the East River, New York City, and easternmost stations are at The Race. (b) Relationship between total dissolved Cu and salinity.

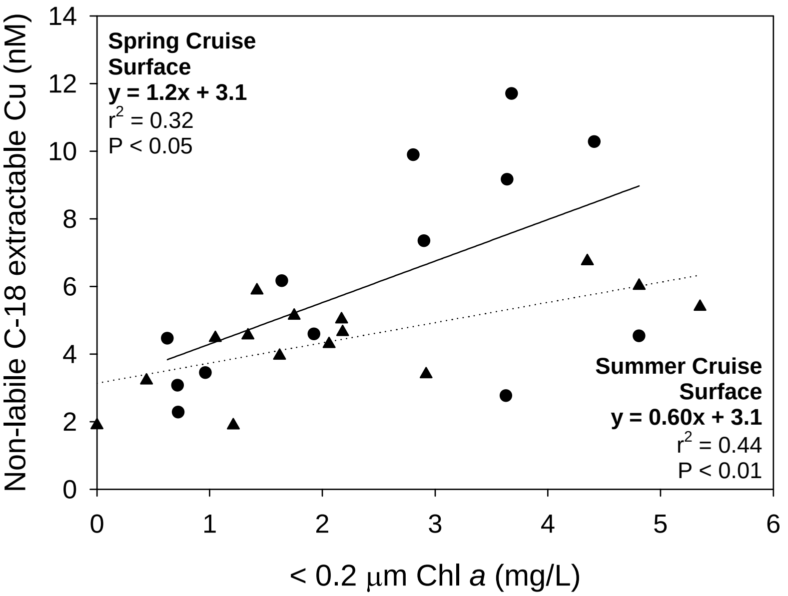

FIGURE 3. Relationship between non-labile organic Cu and small size fraction chlorophyll *a* in surface waters of the LIS. The solid and dotted lines represent linear regressions of spring (circles) and summer (triangles) data, respectively.

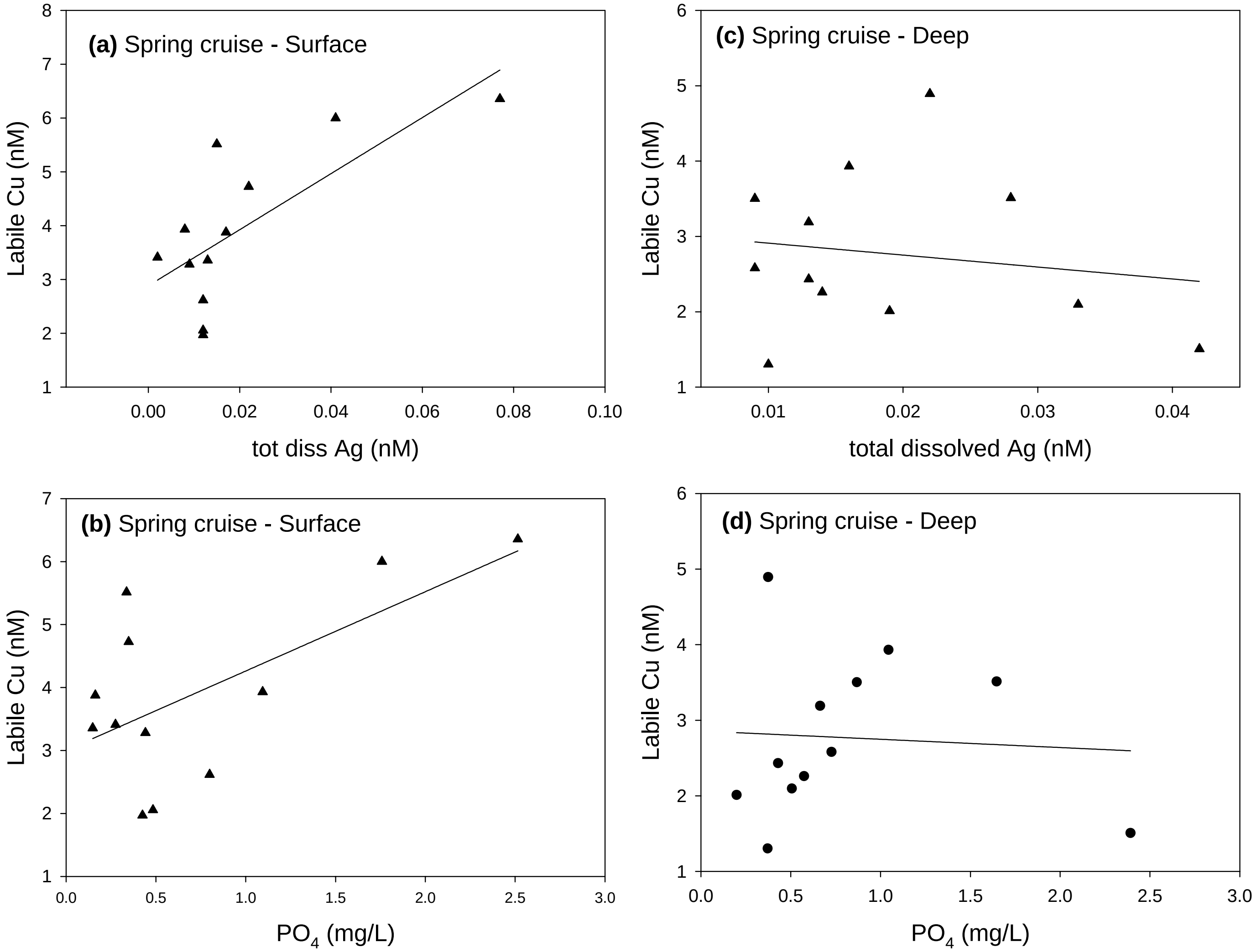

FIGURE 4. Graphs showing relationship between spring season (a) labile Cu and total dissolved Ag in surface waters, (b) labile Cu and dissolved PO_4 in surface waters, (c) labile Cu and total dissolved Ag in deep waters, (d) labile Cu and dissolved PO_4 in deep waters.

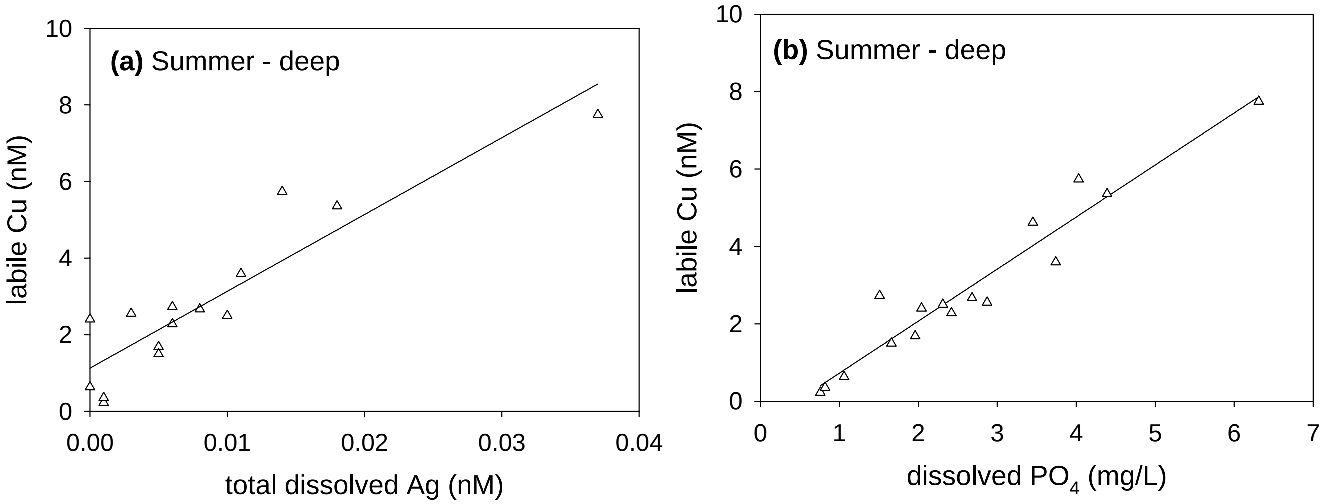

FIGURE 5. Relationship between summer season (a) labile Cu and total dissolved Ag in deep waters, and (b) labile Cu and dissolved PO_4 in deep waters.

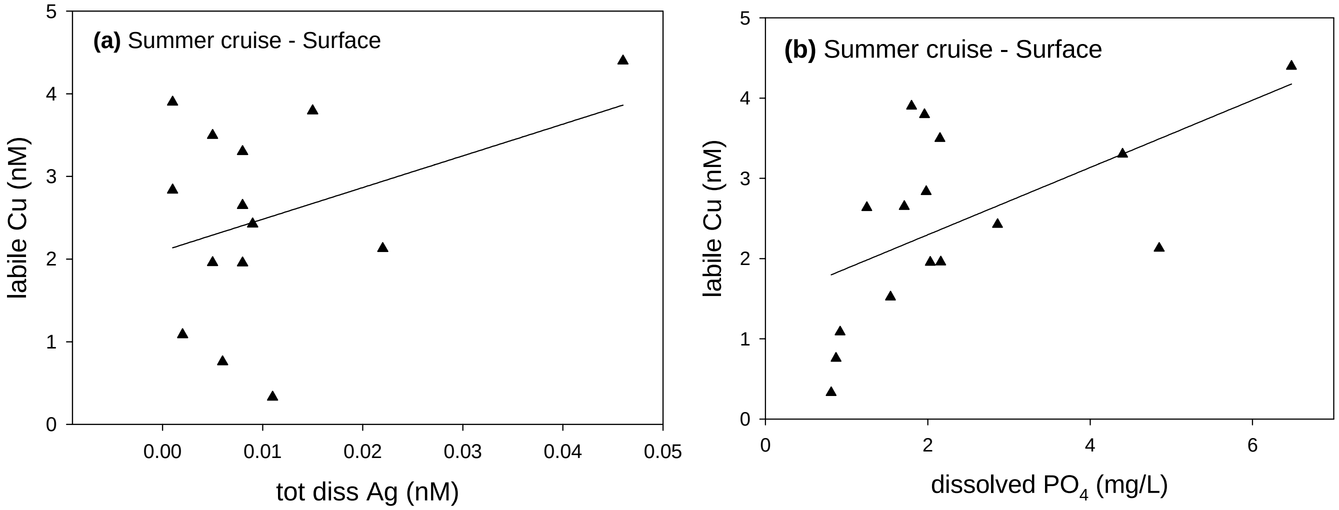

FIGURE 6. Graphs showing relationship between summer season (a) labile Cu and total dissolved Ag in surface waters, (b) labile Cu and dissolved PO_4 in surface waters.

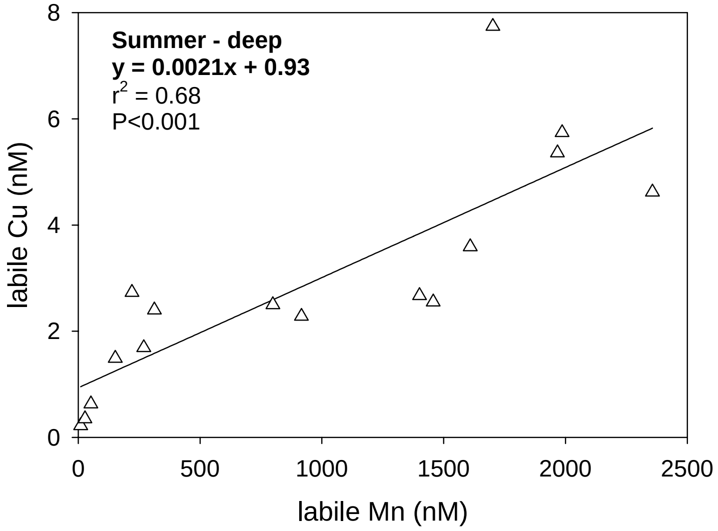

FIGURE 7. Correlation between labile Cu and labile Mn in deep waters of the LIS during the summer cruise. The solid line represents a linear regression of the data.

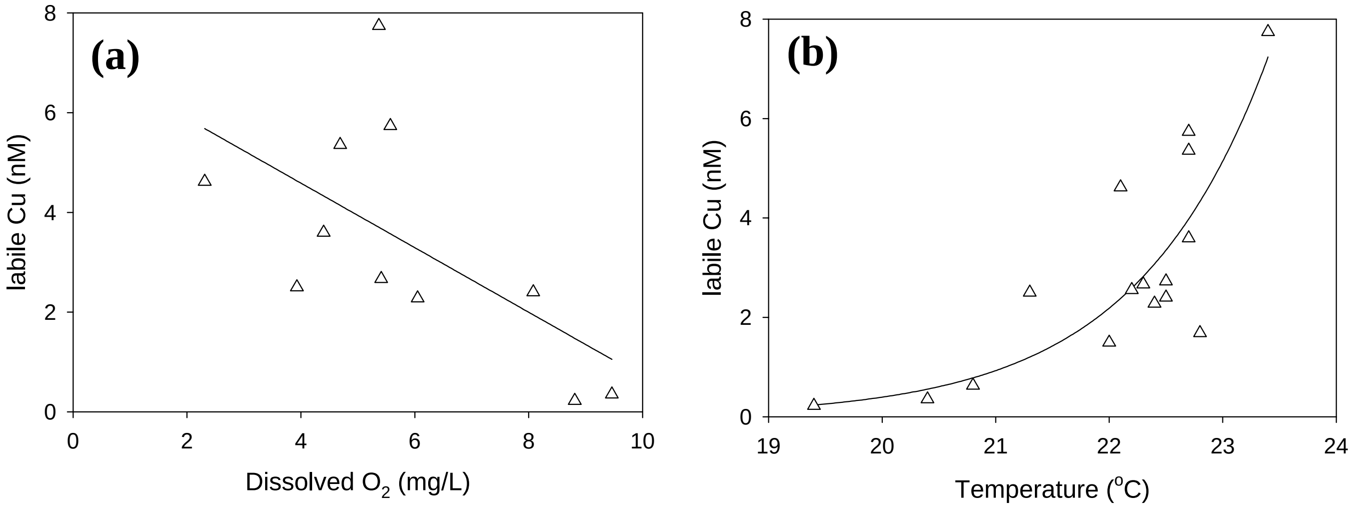

FIGURE 8. Plots of the relationship between labile Cu concentration and water quality parameters: (a) Dissolved oxygen. The solid line represents a linear regression of the data. (b) Temperature. The solid line represents an exponential fit of the data (see text).

Table 1. Station information and ancillary data for spring cruise.

Station ID	Depth	Latitude °N	Longitude °W	Date (mm/dd/yy)	Time (hh:mm)	Temp (°C)	Salinity (psu)	pH	Oxygen (mg/L)	Chl-a (<2.0μm) (μg/L)
1	Surface	41.237	72.053	4/26/05	13:57	7.2	28.6	8.05	9.9	0.72
2	Surface	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
4	Surface	41.165	72.313	4/26/05	9:58	7.6	27.0	8.09	9.9	0.72
5	Surface	41.209	72.909	4/29/05	8:08	8.5	25.1	8.22	9.8	0.96
6	Surface	41.102	72.934	4/29/05	9:39	8.9	25.2	8.31	10.2	0.62
7	Surface	40.981	72.918	4/29/05	11:30	8.7	25.4	8.32	10.3	1.93
8	Surface	41.109	73.253	4/27/05	6:51	9.2	24.5	8.30	10.4	3.63
9	Surface	41.025	73.227	4/27/05	8:18	8.9	25.2	8.34	10.4	1.64
10	Surface	40.931	73.221	4/27/05	10:59	8.4	25.2	8.29	9.5	2.81
11	Surface	41.009	73.514	4/27/05	14:35	8.6	24.8	8.34	10.2	4.41
12	Surface	40.961	73.477	4/27/05	13:14	8.4	24.8	8.34	10.2	3.68
14	Surface	40.935	73.601	4/28/05	7:43	8.6	24.5	8.35	10.4	3.64
15	Surface	40.873	73.734	4/28/05	15:16	8.6	25.7	8.21	7.3	4.81
16	Surface	40.832	73.776	4/28/05	10:45	8.5	24.0	8.13	9.3	2.90
17	Surface	40.804	73.813	4/28/05	11:29	8.8	23.1	8.04	8.5	
18	Surface	40.793	73.899	4/28/05	13:08	10.6	19.9	7.80	7.8	
1	Deep	41.237	72.053	4/26/05	13:57	5.7	30.4	8.04	9.7	0.66
2	Deep	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
4	Deep	41.165	72.313	4/26/05	9:58	7.3	27.7	8.06	9.7	0.98
5	Deep	41.209	72.909	4/29/05	8:08	7.3	25.7	8.16	9.4	0.48
6	Deep	41.102	72.934	4/29/05	9:39	6.0	26.1	8.12	9.4	0.12
7	Deep	40.981	72.918	4/29/05	11:30	8.6	25.4	8.33	10.3	2.07
8	Deep	41.109	73.253	4/27/05	6:51	8.5	25.1	8.30	10.5	1.96
9	Deep	41.025	73.227	4/27/05	8:18	5.2	26.3	8.09	9.7	0.27
10	Deep	40.931	73.221	4/27/05	10:59	7.6	25.4	8.22	9.9	1.72
11	Deep	41.009	73.514	4/27/05	14:35	8.1	25.2	8.27	10.0	3.13
12	Deep	40.961	73.477	4/27/05	13:14	7.3	25.2	8.26	9.8	1.55
14	Deep	40.935	73.601	4/28/05	7:43	6.8	25.4	8.17	9.3	0.36
15	Deep	40.873	73.734	4/28/05	15:16	7.4	25.0	8.18	9.2	1.91
16	Deep	40.832	73.776	4/28/05	10:45	8.3	24.1	8.14	9.2	3.45
17	Deep	40.804	73.813	4/28/05	11:29	8.5	23.4	8.05	8.6	1.80
18	Deep	40.793	73.899	4/28/05	13:08	9.8	21.4	7.88	7.9	0.55

[a] Station 2 not sampled during spring cruise.

Table 1, continued. Station information and ancillary data for summer cruise.

Station ID	Depth	Latitude °N	Longitude °W	Date (mm/dd/yy)	Time (hh:mm)	Temp (°C)	Salinity (psu)	pH	Oxygen (mg/L)	Chl-a (<2.0µm) (µg/L)
1	Surface	72.053	41.237	9/8/05	9:17	20.6	29.2	8.29	6.38	1.21
2	Surface	72.353	41.258	9/8/05	10:01	20.4	29.6	8.27	5.18	0.00
4	Surface	72.313	41.165	9/8/05	13:04	22.0	28.6	8.28	[b]	0.44
5	Surface	72.909	41.209	9/9/05	10:40	22.8	28.9	7.11	[b]	2.17
6	Surface	72.934	41.102	9/9/05	8:45	20.9	27.2	7.13	[b]	1.62
7	Surface	72.918	40.981	9/9/05	7:40	22.6	28.2	7.03	[b]	1.05
8	Surface	73.253	41.109	9/9/05	12:42	23.0	27.4	7.05	[b]	1.34
9	Surface	73.227	41.025	9/7/05	16:49	24.3	26.9	8.21	6.44	2.06
10	Surface	73.221	40.931	9/7/05	15:52	23.6	27.0	8.21	6.50	2.18
11	Surface	73.514	40.009	9/7/05	12:30	23.3	27.0	8.26	7.01	5.35
12	Surface	73.477	40.961	9/7/05	13:17	22.7	26.8	8.19	6.49	1.75
14	Surface	73.601	40.935	9/6/05	13:15	23.4	26.5	8.18	5.01	4.81
15	Surface	73.734	40.873	9/6/05	16:33	23.5	26.3	8.33	8.23	[c]
16	Surface	73.776	40.832	9/7/05	9:21	22.9	25.6	7.73	4.70	4.35
17	Surface	73.813	40.804	9/7/05	8:40	22.9	26.1	7.71	6.00	2.92
18	Surface	73.899	40.793	9/7/05	8:03	23.4	24.8	7.54	3.45	1.42
1	Deep	72.053	41.237	9/8/05	9:17	19.4	30.2	8.25	8.81	0.77
2	Deep	72.353	41.258	9/8/05	10:01	20.4	29.7	8.27	9.46	0.32
4	Deep	72.313	41.165	9/8/05	13:04	20.8	29.4	8.23	[b]	0.68
5	Deep	72.909	41.209	9/9/05	10:25	22.8	27.9	7.04	[b]	0.84
6	Deep	72.934	41.102	9/9/05	9:16	22.0	31.5	7.03	[b]	0.19
7	Deep	72.918	40.981	9/9/05	7:23	22.5	26.2	6.95	[b]	1.05
8	Deep	73.253	41.109	9/9/05	12:58	22.2	28.6	6.78	[b]	0.23
9	Deep	73.227	41.025	9/7/05	16:49	21.3	27.7	7.83	3.93	0.35
10	Deep	73.221	40.931	9/7/05	15:52	22.5	27.1	8.00	8.08	0.55
11	Deep	73.514	40.009	9/7/05	12:30	22.4	27.1	7.98	6.05	1.75
12	Deep	73.477	40.961	9/7/05	13:17	22.3	27.0	7.89	5.41	0.92
14	Deep	73.601	40.935	9/6/05	13:15	22.1	27.1	7.79	2.31	0.61
15	Deep	73.734	40.873	9/6/05	16:33	22.7	26.3	7.80	4.40	2.01
16	Deep	73.776	40.832	9/7/05	9:21	22.7	26.0	7.75	5.57	3.14
17	Deep	73.813	40.804	9/7/05	8:40	22.7	26.4	7.71	4.69	1.66
18	Deep	73.899	40.793	9/7/05	8:03	23.4	24.9	7.57	5.37	1.58

[b] Oxygen sensor failed.

[c] Not detected.

Table 2. Chemical data – spring cruise.

Station ID	Depth	(mm/dd/yy)	Total dissolved Cu (nM)	Chelex-Labile Cu (nM)	Non-labile organic Cu (nM)	Chelex-Labile Mn (nM)	Total dissolved Ag (nM)	Total dissolved PO_4 (mg/L)
1	Surface	4/26/05	6.9	2.06	2.28	66	0.012	0.48
2	Surface	[a]	[a]	[a]	[a]	[a]	[a]	[a]
4	Surface	4/26/05	10.5	1.97	3.07	54	0.012	0.43
5	Surface	4/29/05	13.5	6.66	3.45	287	0.011	0.25
6	Surface	4/29/05	15.8	7.29	4.46	268	0.011	0.20
7	Surface	4/29/05	16.6	6.5	4.59	336	0.008	0.32
8	Surface	4/27/05	13	3.36	2.77	209	0.013	0.15
9	Surface	4/27/05	15.3	3.88	6.16	292	0.017	0.16
10	Surface	4/27/05	14.2	3.28	9.89	279	0.009	0.44
11	Surface	4/27/05	15.7	4.73	10.28	494	0.022	0.35
12	Surface	4/27/05	16.7	5.52	11.7	637	0.015	0.34
14	Surface	4/28/05	16	3.41	9.17	520	0.002	0.28
15	Surface	4/28/05	15.9	2.62	4.53	352	0.012	0.80
16	Surface	4/28/05	21.5	3.93	7.35	486	0.008	1.09
17	Surface	4/28/05	22.6	6.00	8.07	776	0.041	1.76
18	Surface	4/28/05	23.6	6.36	11.21	560	0.077	2.52
1	Deep	4/26/05	4.6	1.3	1.97	24	0.01	0.37
2	Deep	[a]	[a]	[a]	[a]	[a]	[a]	[a]
4	Deep	4/26/05	9.2	2.43	4.56	79	0.013	0.43
5	Deep	4/29/05	14.4	5.22	3.65	195	0.011	0.51
6	Deep	4/29/05	13.4	6.63	4.9	191	0.013	0.82
7	Deep	4/29/05	15.1	5.56	6.5	325	0.024	0.27
8	Deep	4/27/05	13.8	2.01	2.99	181	0.019	0.20
9	Deep	4/27/05	10	3.5	7.01	203	0.009	0.87
10	Deep	4/27/05	15.6	2.1	4.6	217	0.033	0.51
11	Deep	4/27/05	15	4.89	8	445	0.022	0.37
12	Deep	4/27/05	13	2.26	6.55	198	0.014	0.57
14	Deep	4/28/05	12.7	2.58	3.94	327	0.009	0.73
15	Deep	4/28/05	19.4	3.19	8.07	384	0.013	0.66
16	Deep	4/28/05	21	3.93	9.86	533	0.016	1.04
17	Deep	4/28/05	22	3.51	9.2	328	0.028	1.65
18	Deep	4/28/05	17.3	1.51	3.97	371	0.042	2.39

[a] Station 2 not sampled during spring cruise.

Table 2, continued. Chemical data – summer cruise.

Station ID	Depth	(mm/dd/yy)	Total dissolved Cu (nM)	Chelex-Labile Cu (nM)	Non-labile organic Cu (nM)	Chelex-Labile Mn (nM)	Total dissolved Ag (nM)	Total dissolved PO_4 (mg/L)
1	Surface	9/8/05	6.4	0.76	1.89	21	0.006	0.87
2	Surface	9/8/05	6.6	0.33	1.89	23	0.011	0.81
4	Surface	9/8/05	7.9	1.08	3.22	15	0.002	0.92
5	Surface	9/9/05	9.8	3.9	5.02	212	0.001	1.8
6	Surface	9/9/05	8.6	1.52	3.95	4	[c]	1.54
7	Surface	9/9/05	13.8	3.5	4.29	214	[c]	1.25
8	Surface	9/9/05	10.7	1.96	4.55	488	0.005	2.16
9	Surface	9/7/05	14.0	2.64	4.47	208	0.005	2.15
10	Surface	9/7/05	16.1	3.79	5.4	84	0.008	1.71
11	Surface	9/7/05	15.6	2.65	4.65	575	0.015	1.96
12	Surface	9/7/05	13.4	2.84	5.13	605	0.001	1.98
14	Surface	9/6/05	13.5	1.95	6.02	662	0.008	2.03
15	Surface	9/6/05	13.5	2.42	6.05	1120	0.009	2.86
16	Surface	9/7/05	13.5	3.3	6.75	2732	0.008	4.4
17	Surface	9/7/05	14.3	2.13	3.4	1311	0.022	4.85
18	Surface	9/7/05	18	4.4	5.88	1524	0.046	6.48
1	Deep	9/8/05	5.0	0.22	1.08	10	0.001	0.76
2	Deep	9/8/05	6.7	0.35	1.52	28	0.001	0.82
4	Deep	9/8/05	7.1	0.63	2.31	52	[c]	1.06
5	Deep	9/9/05	7.8	1.69	2.94	269	0.005	1.96
6	Deep	9/9/05	6.6	1.49	3.41	152	0.005	1.66
7	Deep	9/9/05	12.8	2.73	5.05	221	0.006	1.51
8	Deep	9/9/05	11.1	2.55	4.59	1457	0.003	2.87
9	Deep	9/7/05	13.0	2.5	4.2	799	0.01	2.31
10	Deep	9/7/05	13.2	2.4	4.37	313	[c]	2.04
11	Deep	9/7/05	14.6	2.28	4.11	916	0.006	2.42
12	Deep	9/7/05	13.1	2.67	4.55	1401	0.008	2.68
14	Deep	9/6/05	13.1	4.62	4.07	2357	[c]	3.45
15	Deep	9/6/05	13.1	3.59	4.54	1609	0.011	3.74
16	Deep	9/7/05	14.3	5.74	4.59	1986	0.014	4.03
17	Deep	9/7/05	13.5	5.36	3.95	1967	0.018	4.39
18	Deep	9/7/05	17.9	7.74	4.78	1702	0.037	6.31

[c] Not detected.

Table 3. Procedural blanks and instrumental detection limits for trace metal analyses. (n) = number of blanks analyzed. Detection limits were calculated as three times the standard deviation of the mean blank.

	Total Dissolved		*Chelex Labile*		*Non-labile Organic*	
	Ag (pM)	**Cu (nM)**	**Cu (pM)**	**Mn (pM)**	**Cu (pM)**	**Mn (pM)**
Spring Cruise						
(n)	6	6	3	3	4	4
Average blank	0.38	0.068	0.025	0.0069	0.12	0.19
s.d.	0.02	0.0017	0.0022	0.0	0.043	0.076
Detection limit	0.06	0.0051	0.007	0.024	0.129	0.228
Summer Cruise						
(n)	6	6	5	5	6	6
Average blank	0.40	0.14	0.19	0	0.14	0.063
s.d.	0.58	0.005	0.027	0.099	0.031	0.027
Detection limit	1.74	0.015	0.081	0.30	0.093	0.081

10. Conclusions:

The results from this project give very useful information on the spatial and temporal distribution of dissolved Cu species in the Long Island Sound, and have provided insight into the processes regulating the Cu distribution. One of the most significant findings was that labile Cu in bottom waters appeared to have a sedimentary source that was driven by low dissolved oxygen levels and high temperatures (>20^{o}C). The sediments in Long Island Sound are a trace metal reservoir that represents the accumulated contamination of the last century or longer. As a consequence, reducing Cu levels in wastewater discharge will probably cause labile Cu concentrations to decrease in surface waters, and will prevent the addition of more Cu contamination to the sedimentary pool; however, such reductions will probably not affect the remobilization of "historical" pollution already contained in the Sound's sediments. We observed a correlation of labile Cu in bottom waters with low dissolved oxygen and increased temperature. Multivariate statistical analysis indicated that temperature was the more important variable. This will probably not affect management decisions, as it will be difficult or impossible to directly affect the bottom water temperatures in the LIS. On the other hand, it may be very useful to continue and perhaps increase research on the subject of rising water temperatures in the Sound. Combined with monitoring of dissolved trace metal levels, this may provide a powerful tool for predicting adverse effects. Finally, the correlation we observed between decreasing dissolved oxygen and increases in labile Cu suggests that some benefit may be had from efforts to increase oxygen levels in the water column. In other words, further reduction of nutrient input and eutrophication may help maintain high levels of oxygen in bottom waters, and may prevent the benthic input of labile or toxic trace metals. Considering the greater influence of temperature on labile Cu, maintaining oxygen levels may not be sufficient for controlling input of labile Cu. Inasmuch as this project provides completely novel trace metal data in the LIS, more research is undoubtedly needed to fully understand the seasonal effects of metal cycling between the sediments and water column.

11. Presentations/Publications/Outreach:

Preliminary data from this study were first presented at the 2005 NY SeaGrant Review Panel Session in Stony Brook, NY (under the title "Temporal and Spatial Changes in Copper Speciation and Toxic Metal Concentrations in the Long Island Sound: Effect of changes in water temperature and dissolved oxygen levels).

Final results were also presented under the same title at the *13th Conference on the Geology of Long Island and Metropolitan New York* on 22 April 2006 at Stony Brook University, and at the *2006 Ocean Sciences Meeting (American Society of Limnology and Oceanography/American Geophysical Union)* on 19-25 February 2006 in Honolulu, HI.

A manuscript with results from this project has been submitted to *Environmental Science and Technology*, and is currently under revision.

12. **Other Information:** Copies of peer-reviewed publications supported by this grant will be submitted to the EPA in the near future.