A WATER QUALITY CRITERIA-BASED EVALUATION OF COPPER IMPACTS TO SOUTH FLORIDA’S FRESHWATER ENVIRONMENT

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ABSTRACT

Copper contamination in south Florida citrus grove soils have led to concerns over the potential impact of copper (Cu) in the aquatic environment. Surface freshwater monitoring data for south Florida were collected from on-line databases to evaluate risk from Cu contamination by comparing those data to water quality criteria (WQC) based on both water hardness and the biotic ligand model (BLM). On average, BLM-based chronic WQC were 1.8 times greater than hardness-based chronic WQC at the same location. As a result, Cu concentrations at 11.8 percent of the sampling stations exceeded hardness-based chronic WQC, while Cu at 1.3 percent of the stations exceeded the BLM-based chronic WQC. Based on the available monitoring data and risk predicted by the BLM, there is a low risk of adverse impact from Cu contamination in the freshwater aquatic community in south Florida.

METHODS

Copper data were queried from the South Florida Water Management District’s DBHYDRO database by county (Broward, Collier, Miami-Dade, Glades, Hendry, Martin, Monroe, Okeechobee, Palm Beach, St. Lucie) and sample collection date (January 1998 – December 2009). Copper concentrations for samples in which Cu was not detected were derived by multiplying the detection limit reported for the sample by a number (0-1) generated by the Random function in Microsoft Excel®. For the purposes of deriving the water quality criteria, DBHYDRO was also queried for total hardness (mg/L $CaCO_3$) and the water quality parameters needed for the BLM (DOC, temperature, pH, calcium, chloride, magnesium, potassium, sodium, total alkalinity, sulfate, and sulfide).

Water hardness (U.S. EPA 1986) and the BLM (Windows Interface, Version 2.2.3, Hydroqual, Inc.) were used to derive WQC. Water quality criteria based on water hardness (mg/L $CaCO_3$) utilized an exponential relationship between water hardness and toxicity:

$$\text{Criterion Maximum Concentration (CMC)} = \exp(0.9422 \times \ln[\text{hardness}] - 1.7) \times 0.96$$
$$\text{Criterion Continuous Concentration (CCC)} = \exp(0.8545 \times \ln[\text{hardness}] - 1.702) \times 0.96 .$$

A single chronic and acute hardness-based WQC was derived for each sampling station for which both Cu and hardness data were available. The data were screened based on water hardness. No WQC were derived for locations at which water hardness exceeded 800 mg/L since those locations were likely to be significantly influenced by marine water. In fact, all of those locations with the elevated hardness were either marine, or were streams and canals likely to be vertically stratified by fresh and salt water.

Never were all of the parameters required by the BLM reported in DBHYDRO for a single sampling event at any sampling station. Therefore, a BLM-based WQC was derived for a sampling station if at least pH, temperature, alkalinity, and two other required parameters were available for that sampling station. Dissolved organic carbon was never measured at any of the stations on the same date as when Cu concentrations were assessed. Therefore, DOC data for all stations in south Florida were utilized for all BLM-based WQC derivations. For the sake of conservatism, the 5th percentile DOC concentration (9.4 mg/L) was the input value. For the other required yet missing parameters, the geometric mean among all sampling stations in south Florida was calculated and entered into the model. Since sulfide was not available in DBHYDRO, a value of 1.0×10^{-9} mg/L was entered into the model per the recommendations of the BLM user’s manual. The BLM is considered appropriate for modeling only acute effects to aquatic organisms. However, the BLM does calculate a CCC by dividing the BLM-derived CMC by an acute-to-chronic ratio of 3.22 (U.S. EPA, 1985).

Freshwater aquatic life should be protected if the 24-hour average and the four-day average concentrations do not respectively exceed the CMC and CCC (U.S. EPA, 2007). The data in DBHYDRO are discrete samples that are best suited individually for evaluation of potential acute impacts by comparison with the CMC. The samples were seldom collected at a frequency that would allow determination of either 24-hour or four-day average concentrations. Therefore, a conservative assumption was made that discrete samples approximated average concentrations for comparison with the derived WQC.

Table 1. Copper concentration (µg/L) data in water by county along with the average acres in citrus production.

County	# of Samples[1]	Percent Detects[2]	Geomean[3]	90th Percentile	Acres in Citrus[4]
Broward	770	53.5	0.24	7.0	1,974
Collier	752	37.2	0.03	2.8	18,776
Miami-Dade	1,953	16.3	0.24	1.8	3,201
Glades	222	45.5	0.25	2.5	5,959
Hendry	218	44.0	0.05	3.3	55,246
Martin	618	89.2	4.53	16.3	37,711
Monroe	105	77.1	0.62	2.1	0
Okeechobee	132	68.2	0.54	3.0	7,301
Palm Beach	2,495	58.0	0.10	4.4	11,215
St. Lucie	868	77.2	2.25	7.6	76,456

1 Number of samples collected from county between 1998 and 2008 that were analyzed for copper.
2 The percentage of collected samples in which copper was detected.
3 Data for samples in which Cu was not detected were included in the calculation of the average concentrations. Concentrations for the non-detect samples were derived by multiplying the detection limit reported for the sample by a number generated by the Random function in Microsoft Excel®. Method detection limits ranged from 0.0012 to 3,700 µg/L.
4 Average of acreages reported for years 1966, 1969, 1975, 1980, 1985, 1990, 1998, 2000, 2006, and 2008 (Citrus Summary reports, Florida Department of Agriculture and Consumer Services).

Figure 1. Water quality data (hardness, alkalinity, dissolved organic carbon) by county for samples collected between 1998 and 2009.

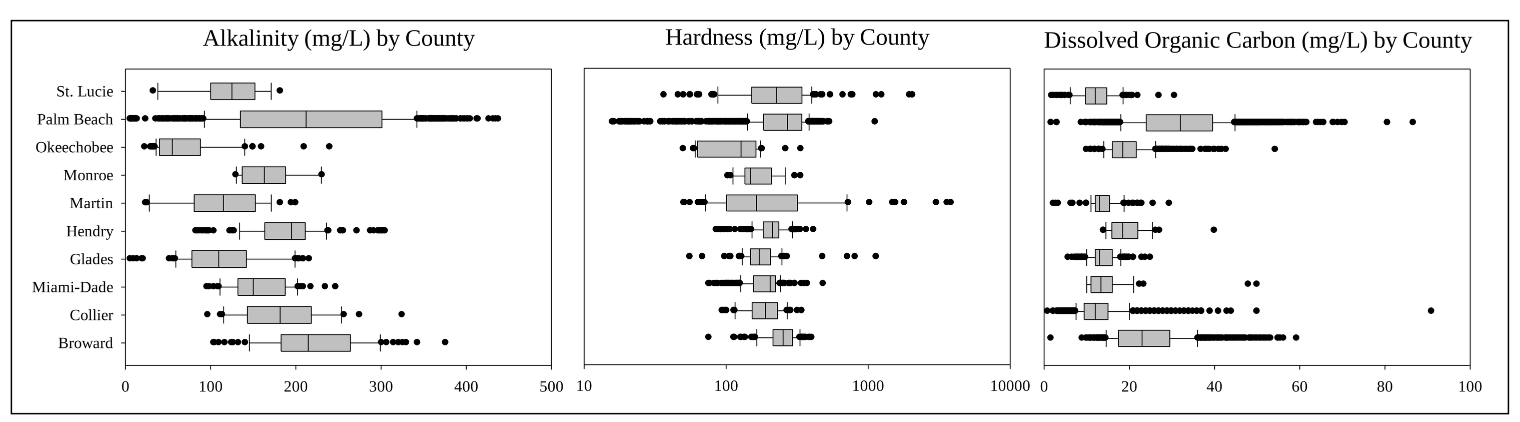


Figure 2. Nationally recommended (USEPA) hardness-based water quality criteria relative to the cumulative distribution for the average copper concentrations for individual sampling stations in south Florida.

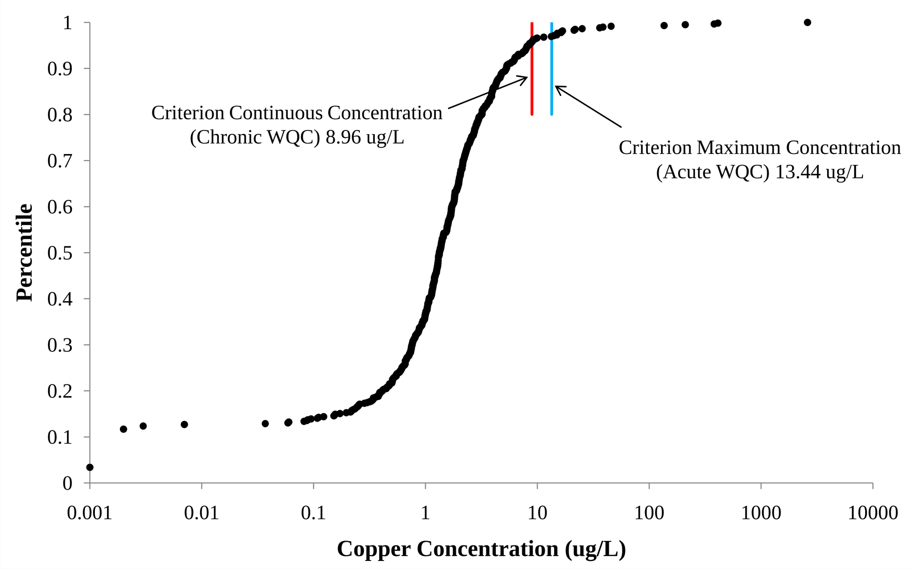


Figure 3. Derived site specific water quality criteria (WQC). Graph A is a comparison of the co-located hardness and BLM-based site specific WQC. Graph B shows the county-wide average hardness-based WQC while Graph C shows the county-wide average BLM-based WQC.

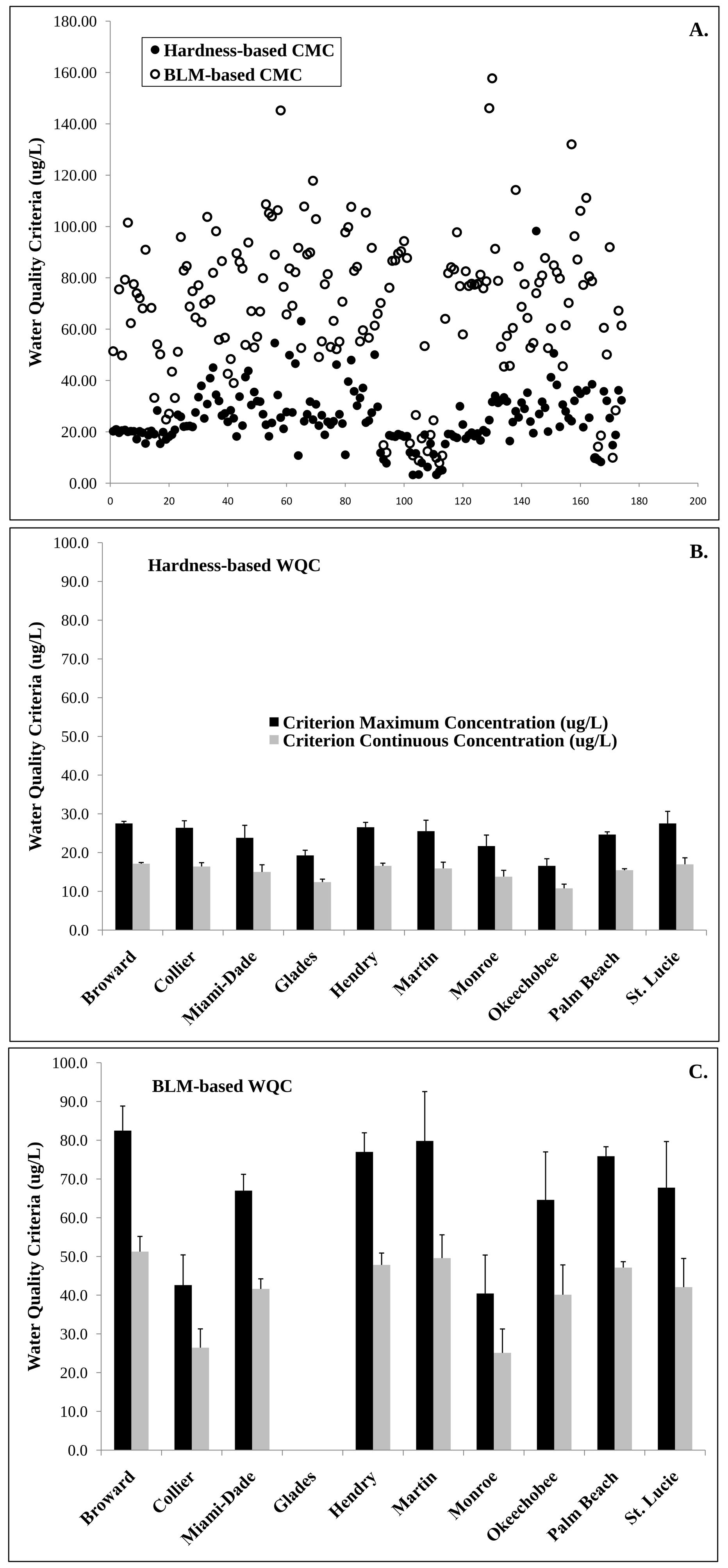
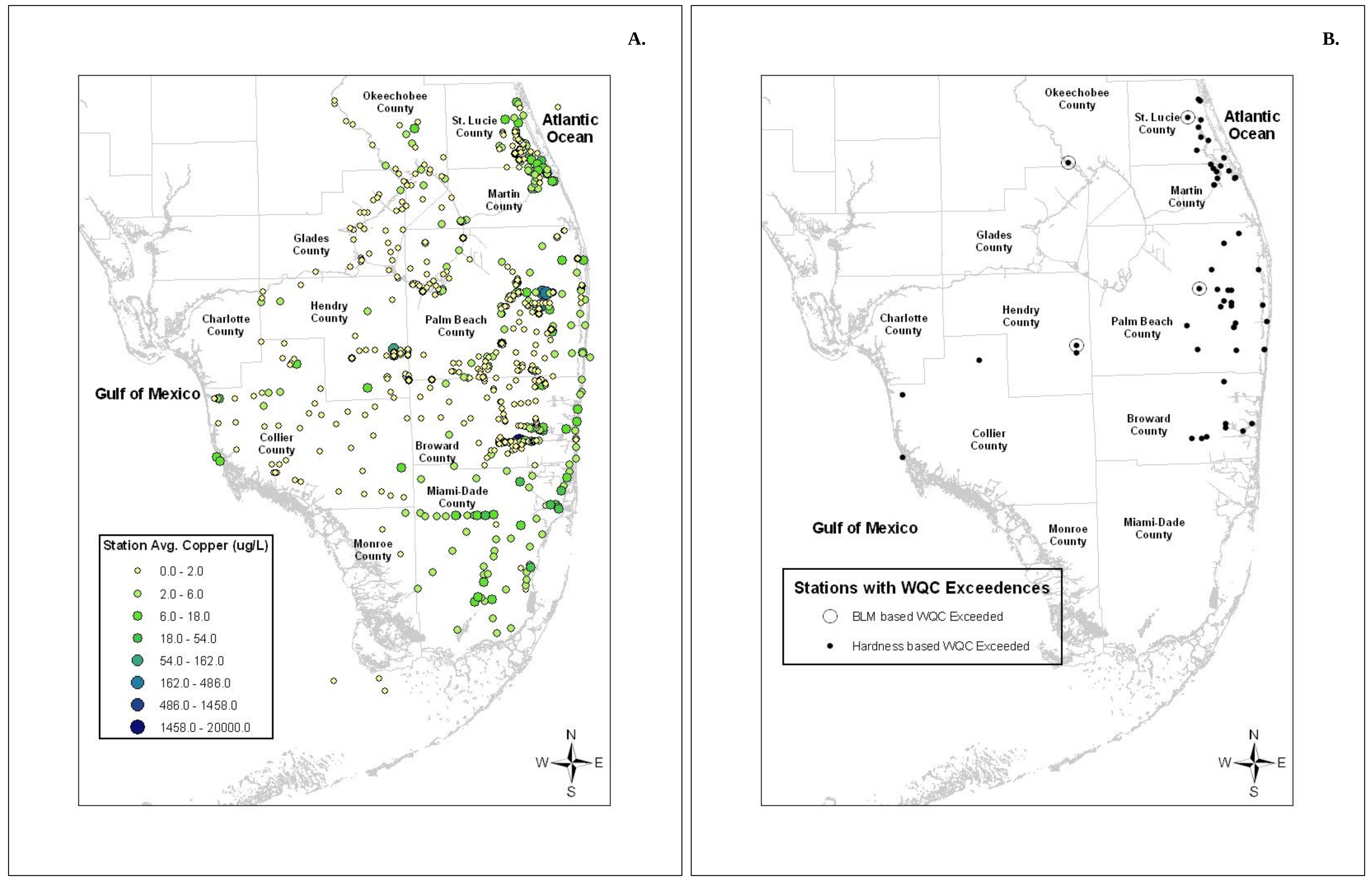


Figure 4. Locations in south Florida from which the surface water samples analyzed for copper were collected between 1998 and 2009. Graph A shows the location of the sampling stations along with the average copper concentration for those stations. Graph B shows the stations at which copper concentrations in single samples exceeded the site-specific hardness or BLM-based water quality criteria.



DISCUSSION

- Table 1 shows Cu data, by county, for the 8,133 samples that were collected from the sampling stations and analyzed for Cu between 1998 and 2008. The combination of the geometric mean Cu concentration by county, percent of samples with detectable Cu, and 90th percentile concentrations indicate that surface waters in Martin and St. Lucie counties were the most contaminated by Cu.
- Figure 1 shows, by county, data for the water quality parameters of alkalinity, hardness, and dissolved organic carbon, all of which have significant roles in determining the bioavailability of Cu in water. Copper bioavailability and the correlated toxicity vary inversely with each of these parameters.
- Figure 2 compares the generally recommended (USEPA) hardness-based WQC for Cu (CCC = 8.96 µg/L; CMC = 13.44 µg/L) to the average Cu concentrations for all of the sampling stations. The assumed water hardness for the recommended WQC was 100 mg/L, which is softer than the hardness at most of the stations in south Florida (229 mg/L), indicates that it is too conservative for south Florida emphasizing the need to evaluate Cu risk based on local conditions.
- Figure 3 shows three graphs pertaining to the site-specific WQC. Graph 3A compares the co-located derived site-specific hardness and BLM-based WQC. On average, the BLM-based WQC was 2.9 times greater than the co-located hardness-based WQC indicating that predicting risk for Cu at a location based on the BLM-based WQC is less likely compared to risk based on the hardness-based WQC. Graphs 3B and 3C show the average derived hardness (3B) and BLM-based (3C) WQC by county. The hardness-based WQC were remarkably consistent among the counties (average CMC = 28.95 µg/L [SE=1.03]; average CCC = 17.7 µg/L [SE=0.53]) while the BLM-based WQC were much more variable. Copper concentrations in approximately 2 percent of the samples exceeded the respective site-specific hardness-based CCC while concentrations in less than 1 percent of the samples exceeded site-specific hardness-based CMC. The fact that the site-specific BLM-based WQC are greater than the hardness-based WQC means that an even lower percentage of Cu concentrations exceeded the BLM-based WQC.
- Figure 4 contains two graphs showing the locations of the sampling stations along with the average Cu concentration for those stations (Graph 4A) and the stations where concentrations exceeded the site specific hardness or BLM-based WQC (Graph 4B).
- Under a presumption that citrus agriculture would have a significant role in Cu contamination detected in surface waters, county-based average acreage in citrus production is also shown in Table 1. The averages are of data reported for those counties for the years of 1966, 1969, 1975, 1980, 1985, 1990, 1998, 2000, 2006, and 2008 as reported by the Florida Department of Agriculture and Consumer Services. However, only a weak positive relationship ($r^2 = 0.27$) was evident between acreage in citrus production and the percentage of samples with detectable Cu. Other potential Cu sources in south Florida include natural background Cu in soils, Cu-based pesticides, and Cu-treated landscaping timbers and Cu-piping in residential areas. A study designed to assess the role of the various Cu sources in the contamination of south Florida’s water would be necessary to find a more causative relationship.
- Based on the available data, there does not appear to be a current significant risk to aquatic communities in south Florida on a large scale. Given that Cu concentrations locally can be excessive (> 1,000 ug/L), there is a significant local risk from Cu contamination.

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