An Assessment of Metals in Estuarine Water using Clean Hand Techniques

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Abstract: Assessment of metals in estuarine water is complicated by factors such as field sampling and analytical issues with contamination, and the influence of other water quality attributes that influence the partitioning and toxicity of metals. In the Delaware Estuary, copper concentrations continue to be near water quality criteria with several apparent exceedances of the marine criteria in the vicinity of Pea Patch Island (RM 60.6) in a recent assessment. The DRBC performed additional data collection for copper, zinc and nickel using enhanced analytical methods EPA Method 200.8, modified collection procedures and changes in the spatial scale of sampling in segments of the Delaware River which have exhibited apparent copper exceedances. Samples were collected at six existing Boat Run sampling locations from Reedy Island (RM 55) to Marcus Hook (RM 80.3) and an additional five monitoring stations between each of these existing stations. Ancillary parameters and field measurements were analyzed and collected in support of this efforts. Surface and bottom samples were collected for metals, and analyzed for the total and dissolved fractions. Three sampling events in the Fall of 2011, and the Spring and Summer of 2012 were implemented using Clean Hands/Dirty Hands techniques to reduce contamination associated with sample collection. Analyses were conducted utilizing high resolution analytical techniques (ICP/MS) EPA Method 200.8 and clean lab procedures to reduce analytical contamination. Method Detection Limits (MDLs) achieved were between 1 and 2 orders of magnitude lower than those achieved previously using EPA Method 200.7. Median MDLs ranged from 0.02 to 0.08 ug/. Furthermore, median equipment rinsate blank results were 0.12, 0.09 and 0.42 ug/L for Copper, Nickel and Zinc, respectively. This combination of enhanced analytical techniques and Clean Hands sample collection methods reduces MDLs and provides cleaner blanks, thereby increasing the range of detectable concentrations which reduces uncertainties and enhances assessment.

Equipment Checklist

- ❑Sample Bottles, laboratory provides pre-cleaned 500 ml HDPE sample collection bottles which are double bagged
- ❑Deionized Water, laboratory provides DI water for rinsate blank
- ❑5% HCl (reagent grade), Soap (Alconox 3% solution), and additional DI water for equipment decontamination during sampling
- ❑0.45 um filter (proofed), filtering for dissolved fraction
- ❑Nitric acid (ultra trace metals grade), as a preservative
- ❑Peristaltic pump and new Masterflex tubing, for surface sample collection
- ❑5L Niskin Bottle, for bottom sample collection

Pre-clean all sampling equipment including tubing, Niskin with Alconox, DI water and HCl and double bag for transport to the field. Teflon spray coat all exposed metal pieces on Niskin.

Sampling (3 Person Crew)

DH=Dirty Hands (2)
CH=Clean Hands (1) Double gloved

Bottom Sampling

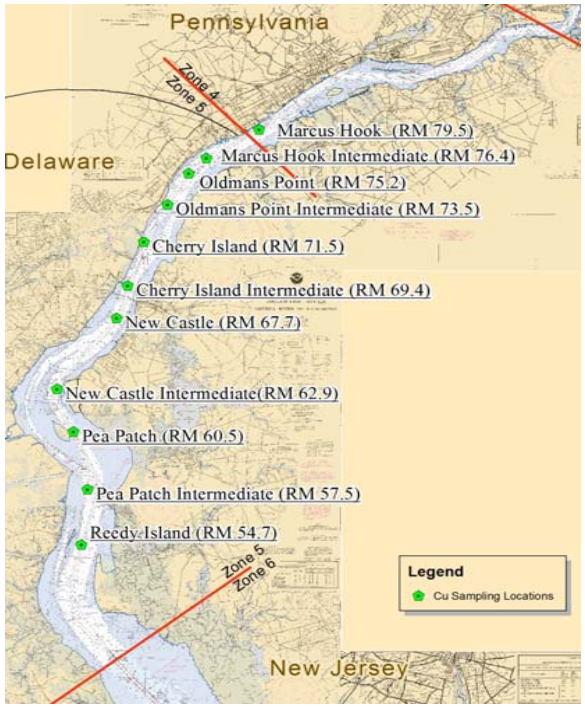
Surface Sampling

Non-Filtered Sample Collection

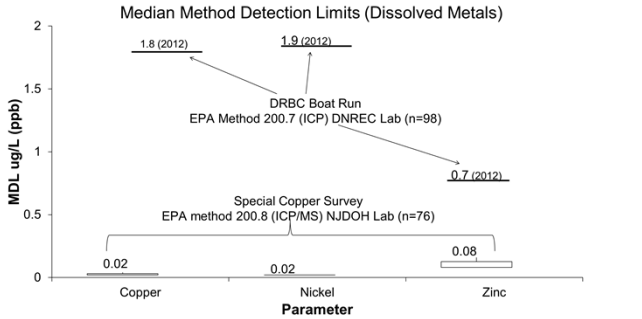
Filtering Sample Collection

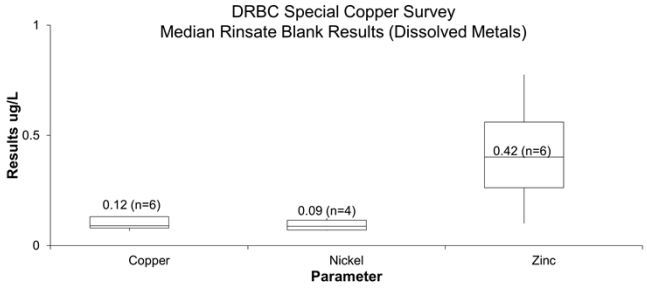
Sampling Steps

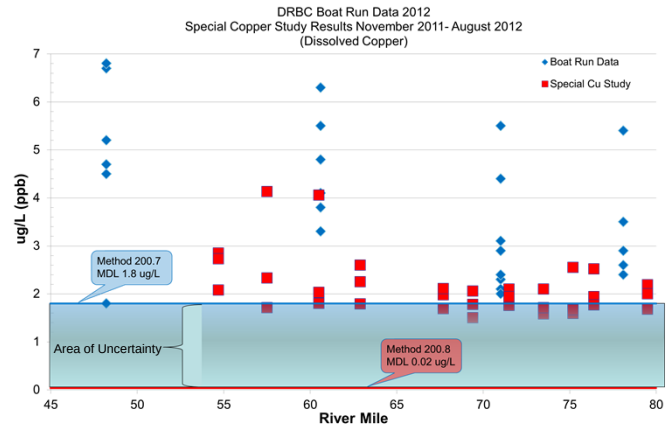
1. DH1 prepares sampling equipment (Niskin) and deploys and retrieves sampler
2. DH2 removes the bag containing the sample tubing from the container
3. DH2 opens the outer bag.
4. CH opens inner bag and removes one piece of tubing not allowing tubing to touch anything.CH places the tubing into the peristaltic pump and DH2 secures it there
5. DH1 brings the Niskin to the area containing the peristaltic pump.
6. CH attaches one end of the tubing to the nipple on the Niskin, only touching the tubing while doing so.
7. DH2 opens the container with the double-bagged sample bottle for metals.
8. CH opens the inner bag and takes out one of the sample bottle
9. DH2 completes the label for the first sample, and hands it to the CH to put on the bottle. DH2 apply clear tape while CH holds the labeled sample bottle.
10. CH opens the lid to fill the bottles in the order identified below
11. CH holds the discharge end of the tubing over the sample bottle and tells DH2 to turn on pump
12. CH rinses samples bottles using sampled water
13. CH fills sample bottles in the following order:
    - 500 ml total Zn, Cu, Ni, Cd (nitric)
    - 500 ml dissolved Zn, Cu, Ni, Cd (nitric)
14. Prior to collection of the dissolved sample, DH2 take out the filter and open the bag. CH removes the filter from bag and attaches it to the outlet end of the tubing.
15. As each sample bottle is filled i.e. total and dissolved metals, DH1 turns off the pump
16. DH2 adds the nitric acid for preservation for total and dissolved metals for each at 1ml per 500 ml
17. CH tightly caps each sample bottle DH2 holds the outside bag open and CH places the bottle into the inside bag, and seals the inside bag.
18. DH2 reseals the outside bag and places it in the sample storage cooler



Lab Parameter	Method
Specific conductance	SM2510B
Hardness, as CaCO3	200.7
Sodium	200.7
Calcium	200.7
Magnesium	200.7
Potassium	200.7
Copper (dissolved and total)	200.8
Nickel (dissolved and total)	200.8
Zinc (dissolved and total)	200.8
Cadmium (dissolved and total)	200.8
Sulfate	300.0
Total Alkalinity	SM 2320B
Chloride	300.0
Dissolved Organic Carbon	SM 5310C
Total Organic Carbon	SM 5310C
Total Suspended Solids	SM2540D
pH	SM 4500H+ B
Sulfide	Orion Sulfide Electrode







Conclusions:

- ❑ DRBC's existing Boat Run Survey uses conventional sampling and analytical techniques (Method 200.7) and achieved a DL of 1.8 ug/L for dissolved copper
- ❑ The Special Copper Survey used Clean Hands and enhanced analytical techniques (Method 200.8) and achieved a DL of 0.02 ug/L for dissolved copper
- ❑ Elevated DLs using Method 200.7 increase analytical uncertainty and hinder assessment
- ❑ A combination of Clean Hands/Dirty hands sample collection methods and an enhanced analytical technique, Method 200.8, achieved lesser contamination issues and lower detection limits, and therefore provide a more accurate assessment