Assessment for Metals data in Delaware

All available data for the dissolved forms of copper, lead and zinc in the period from September 2008-August 2013 were compiled. The Department has selected sampling station locations that are statistically different from each other (and thus, eliminated duplicative stations) in the past as a way to more effectively use sampling dollars. The Department usually has more than one station in a watershed to help assess fate and transport of various compounds of interest. Thus, for 305(b) assessment purposes, the Department assessed each station as an individual segment. The Department is working with EPA to align segments with these ideas in mind, and expects to complete that work by the 2016 Integrated Report cycle.

A table of the metals data was prepared that also included salinity and hardness values for each sample date and location. Any lab data below reporting levels were not carried forward in the analysis. This eliminated lead for more detailed analysis for the period considered as no data was available above laboratory reporting levels. For samples taken in fresh waters (salinity values below 5 ppt at the time of sampling) chronic and acute criteria were calculated using the hardness-dependent formulas in Delaware's Surface Water Quality Standards. The hardness concentration reported at the time of sampling was used in the calculation. Samples taken in marine waters were compared to the constant values for acute criteria in the water quality standards. Reported metals concentrations were divided by the associated criteria values on a station-by-station, day-by-day basis and converted to percentages of the criteria. Values less than 100% were below the applicable criterion, and that station sampling event was removed from further consideration. Following a comparison of the measured metal concentration to the calculated criteria as described above, values greater than 100% were sorted by station and date. Stations with only one station sampling event greater than 100% for any magnitude portion of the criteria in the period were eliminated from further consideration. This was done because, by definition, 2 or more exceedances within a three year period are required to be considered sufficient to possibly impact aquatic life. Because of differences in averaging periods between acute and chronic criteria, acute criteria were considered first. If two or more sampling events at the same station for the same metal were above 100% of the criteria in a three year period, those stations were placed on the 303(d) list as failing to support the aquatic life use. If two or more exceedances of the acute criteria were sufficient to cause a 303(d) listing, chronic criteria were not further evaluated for the same station and metal.

Table 1 Stations with more than one sampling event above 100% of acute critieria

Station ID	date	Salinity	Fresh or Marine	Hardness	Copper (ug/l)	Zinc (ug/l)	Copper chronic criteria	Copper acute criteria	Zinc Chronic criteria	Zinc acute criteria	% Copper chronic criteria	% Copper acute criteria	%Zn Chrnoic Criteria	% Zn Acute Criteria
311041	5/18/2010	0.1	F	33.1	5.6	28.3	3.5	4.7	46.3	45.9	160.8%	118.1%		
311041	1/17/2012	0.1	F	66.0	7.3	31.9	6.3	9.1	83.1	82.4	116.3%	80.3%		
311041	4/10/2012	0.1	F	59.8	9.2	17.4	5.8	8.3	76.4	75.8	159.4%	111.1%		
316031	11/19/2008	1.0	F	23.9		47.4	2.6	3.5	35.1	34.8			134.9%	136.0%
316031	11/10/2009	1.0	F	19.8		34.6	2.2	2.9	30.0	29.7			115.3%	116.3%
316031	12/15/2009	1.0	F	19.2		29.4	2.2	2.8	29.2	28.9			100.7%	101.6%
316031	2/7/2011	1.0	F	19.4		40.3	2.2	2.9	29.4	29.2			136.7%	137.8%
316031	3/7/2011	1.0	F	21.2		34.3	2.4	3.1	31.7	31.5			108.1%	109.0%
316031	4/18/2011	1.0	F	21.2		32.1	2.4	3.1	31.7	31.5			101.1%	102.0%
316031	12/5/2011	1.0	F	15.1		26.1	1.8	2.3	23.8	23.6			109.4%	110.3%
316031	2/14/2012	1.0	F	12.9		22.7	1.6	2.0	20.8	20.7			109.0%	109.8%
316031	12/12/2012	1.0	F	20.9		36.4	2.4	3.1	31.4	31.1			116.1%	117.0%
316031	2/19/2013	1.0	F	20.3		36.7	2.3	3.0	30.6	30.3			120.0%	120.9%
109091	5/8/2012	7.0	M	1350.0	6.5		3.1	4.8	81.0	90.0		135.4%		
109091	8/7/2012	6.7	M	1300.0	5.6		3.1	4.8	81.0	90.0		116.7%		
206091	6/20/2011	6.2	M	1163.3	7.2		3.1	4.8	81.0	90.0		150.0%		
206091	8/10/2011	17.1	M	3212.5	5.7		3.1	4.8	81.0	90.0		118.2%		
206091	6/11/2012	8.2	M	1650.0	6.0	18.7	3.1	4.8	81.0	90.0		125.0%		
206091	7/16/2012	11.7	M	2270.0	8.0		3.1	4.8	81.0	90.0		166.7%		
206091	8/13/2012	9.2	M	1750.0	7.8		3.1	4.8	81.0	90.0		162.5%		
206101	9/13/2010	25.2	M	4670.0	10.9		3.1	4.8	81.0	90.0		226.0%		
206101	3/14/2011	18.3	M	3370.0	5.3		3.1	4.8	81.0	90.0		110.4%		
206101	6/20/2011	24.0	M	4430.0	5.3		3.1	4.8	81.0	90.0		109.7%		
206101	5/7/2012	24.4	M	4680.0	6.5		3.1	4.8	81.0	90.0		135.4%		
206101	6/11/2012	22.4	M	4730.0	9.2	33.2	3.1	4.8	81.0	90.0		191.7%		

Station ID	date	Salinity	Fresh or Marine	Hardness	Copper (ug/l)	Zinc (ug/l)	Copper chronic criteria	Copper acute criteria	Zinc Chronic criteria	Zinc acute criteria	% Copper chronic criteria	% Copper acute criteria	%Zn Chrnoic Criteria	% Zn Acute Criteria
206101	7/16/2012	26.1	M	5170.0	9.8		3.1	4.8	81.0	90.0		204.2%		
206101	8/13/2012	27.7	M	5180.0	9.1		3.1	4.8	81.0	90.0		189.6%		
206101	12/5/2012	14.8	M	2830.0	5.6		3.1	4.8	81.0	90.0		116.7%		
206141	6/20/2011	15.1	M	2786.7	5.1		3.1	4.8	81.0	90.0		106.3%		
206141	6/11/2012	15.4	M	3270.0	7.2	28.1	3.1	4.8	81.0	90.0		150.0%		
206141	7/16/2012	19.4	M	3840.0	9.9		3.1	4.8	81.0	90.0		206.3%		
206141	8/13/2012	16.7	M	3290.0	7.8		3.1	4.8	81.0	90.0		162.5%		
206141	9/11/2012	13.9	M	2630.0	5.2		3.1	4.8	81.0	90.0		108.3%		
206231	8/10/2011	20.9	M	3853.3	5.2		3.1	4.8	81.0	90.0		108.3%		
206231	6/11/2012	6.9	M	1450.0	6.4	22.7	3.1	4.8	81.0	90.0		133.3%		
206231	7/16/2012	13.2	M	2560.0	8.5		3.1	4.8	81.0	90.0		177.1%		
206231	8/13/2012	8.1	M	1530.0	7.3		3.1	4.8	81.0	90.0		152.1%		
305011	9/16/2010	29.5	M	5450.0	13.1		3.1	4.8	81.0	90.0		271.9%		
305011	12/13/2011	20.8	M	3810.0	9.6		3.1	4.8	81.0	90.0		200.0%		
305011	3/20/2012	24.8	M	4750.0	13.0	16.1	3.1	4.8	81.0	90.0		270.8%		
305011	5/15/2012	25.7	M	4870.0	9.5	13.5	3.1	4.8	81.0	90.0		197.9%		
305041	9/16/2010	28.5	M	5220.0	5.9		3.1	4.8	81.0	90.0		122.9%		
305041	12/13/2011	23.5	M	4400.0	9.6		3.1	4.8	81.0	90.0		199.0%		
305041	3/20/2012	27.6	M	5190.0	6.0	12.9	3.1	4.8	81.0	90.0		125.0%		
305041	5/15/2012	26.8	M	5020.0	8.4	13.0	3.1	4.8	81.0	90.0		175.0%		
306091	12/13/2011	28.2	M	5230.0	9.3		3.1	4.8	81.0	90.0		193.8%		
306091	5/15/2012	30.4	M	5920.0	7.5	12.9	3.1	4.8	81.0	90.0		156.3%		
306111	12/13/2011	27.9	M	5220.0	9.3		3.1	4.8	81.0	90.0		193.8%		
306111	3/20/2012	30.2	M	5770.0	5.6	13.4	3.1	4.8	81.0	90.0		115.6%		
306111	5/15/2012	30.6	M	5805.0	7.8	12.7	3.1	4.8	81.0	90.0		161.5%		
306121	6/16/2010	29.5	M	5420.0	5.0		3.1	4.8	81.0	90.0		104.2%		

Station ID	date	Salinity	Fresh or Marine	Hardness	Copper (ug/l)	Zinc (ug/l)	Copper chronic criteria	Copper acute criteria	Zinc Chronic criteria	Zinc acute criteria	% Copper chronic criteria	% Copper acute criteria	%Zn Chrnoic Criteria	% Zn Acute Criteria
306121	9/16/2010	31.0	M	5750.0	5.5		3.1	4.8	81.0	90.0		114.6%		
306121	12/13/2011	27.6	M	5190.0	8.5		3.1	4.8	81.0	90.0		177.1%		
306121	5/15/2012	30.8	M	5760.0	8.8	14.0	3.1	4.8	81.0	90.0		183.3%		
306181	9/16/2010	20.7	M	3800.0	6.3		3.1	4.8	81.0	90.0		131.3%		
306181	12/13/2011	19.4	M	3610.0	7.9	22.6	3.1	4.8	81.0	90.0		164.6%		
306181	4/11/2012	15.5	M	3020.0	5.7	10.9	3.1	4.8	81.0	90.0		118.8%		
306181	5/15/2012	17.8	M	3310.0	10.0		3.1	4.8	81.0	90.0		208.3%		
306181	6/19/2012	20.8	M	4230.0	5.5		3.1	4.8	81.0	90.0		114.6%		
306331	12/13/2011	19.7	M	3710.0	9.1	12.2	3.1	4.8	81.0	90.0		189.6%		
306331	5/15/2012	22.8	M	4250.0	8.2		3.1	4.8	81.0	90.0		170.8%		
306341	12/13/2011	14.0	M	2540.0	8.2		3.1	4.8	81.0	90.0		170.8%		
306341	5/15/2012	21.6	M	4070.0	7.8		3.1	4.8	81.0	90.0		162.5%		
308051	9/14/2010	14.2	M	2605.0	11.1	21.4	3.1	4.8	81.0	90.0		230.2%		
308051	12/12/2011	22.5	M	4205.0	10.1		3.1	4.8	81.0	90.0		209.4%		
308051	3/19/2012	16.5	M	3210.0	5.4		3.1	4.8	81.0	90.0		112.5%		
308051	6/18/2012	21.7	M	4565.0	6.0		3.1	4.8	81.0	90.0		124.0%		
310011	11/14/2011	23.0	M	4350.0	6.3		3.1	4.8	81.0	90.0		131.3%		
310011	12/12/2011	23.3	M	4560.0	10.0		3.1	4.8	81.0	90.0		208.3%		
310031	11/14/2011	7.0	M	1250.0	5.0		3.1	4.8	81.0	90.0		104.2%		
310031	7/30/2012	19.3	M	3720.0	5.1		3.1	4.8	81.0	90.0		106.3%		
312011	12/12/2011	24.7	M	4980.0	10.4		3.1	4.8	81.0	90.0		216.7%		
312011	5/14/2012	22.1	M	4305.0	5.0		3.1	4.8	81.0	90.0		103.1%		

Table 2 Summary table of Stations from Table 1 with 303(d) listings for Aquatic Life Use impairments for metals

Station	Watershed	Location	Metal of Concern	# Events Over Acute Criteria
109091	Appoquinimink River	Delaware River (Appoquinimink at Mouth)	Copper	2
206091	Murderkill River	US Rt. 113 at Frederica By-Pass	Copper	5
206101	Murderkill River	Bowers Beach Wharf	Copper	8
206141	Murderkill River	3.25 miles from the mouth	Copper	5
206231	Murderkill River	Confluence of Kent County STP trib.	Copper	4
305011	Lewes and Rehoboth Canal	Canal Rt. 1	Copper	4
305041	Lewes and Rehoboth Canal	Lewes and Rehoboth Canal at Rd. 18 Bridge	Copper	4
306091	Rehoboth Bay	Buoy 7, Rehoboth Bay	Copper	2
306111	Rehoboth Bay	Massey's Ditch at Buoy 17	Copper	3
306121	Indian River	Buoy 20, Indian River Bay	Copper	4
306181	Indian River	Buoy 49, Indian River	Copper	5
306331	Indian River	Island Creek mouth	Copper	2
306341	Indian River	Island Creek, upper third	Copper	2
308051	Rehoboth Bay	Guinea Creek at Rt. 298 Bridge	Copper	4
310011	Little Assawoman Bay	Little Assawoman Bay Ditch at Rd. 58 Bridge	Copper	2
310031	Little Assawoman Bay	Dirrickson Creek, Rd. 381	Copper	2
311041	Buntings Branch	Buntings Branch at Rt. 54	Copper	3
312011	Indian River	White Creek at the mouth of Assawoman Canal	Copper	2
316031	Nanticoke River	Gravelly Branch at Deer Forest Road (Rd 565) on west edge of Redden State Forest Jester Tract	Zinc	10

For chronic criteria in fresh waters, sampling events above 100% of the criteria were considered as possible exceedances of the applicable criterion. Values greater than 100% are only considered possible exceedances because they address only the magnitude component of the criteria. Water quality criteria also contain duration and frequency components that need to be properly considered. All three components of the criteria (magnitude, duration and frequency) must be exceeded to qualify as a confirmed violation for chronic criteria. This is discussed below.

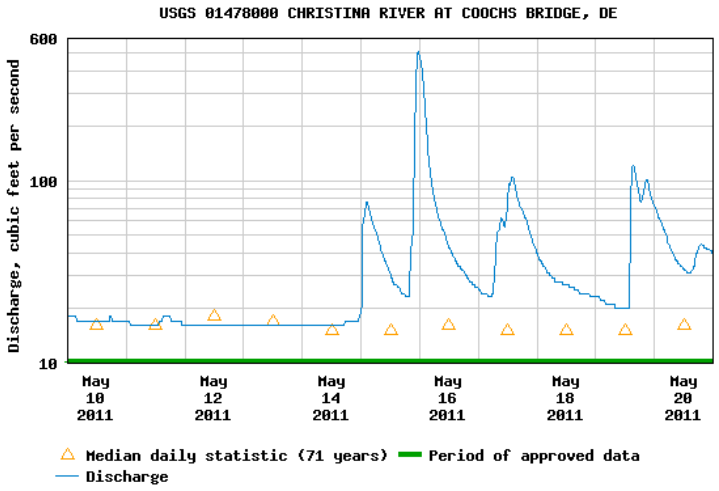
We next considered the duration that the reported concentration is expected to have sustained. This is important because chronic aquatic life criteria are four-day average values, while routine sampling involves the collection of instantaneous grab samples. A key question is whether the result of an instantaneous grab is representative of a four-day average. If environmental conditions were stable for a four-day period prior to sample collection, then an instantaneous grab sample result can be compared to a four-day average criterion with increased confidence. For this reason, it is inappropriate to compare a single grab sample to chronic criteria in tidal marine waters. A primary driver in determining whether environmental conditions were stable prior to sampling is stream or tidal flow. Flow impacts dilution and therefore concentration. Flow can also have an important effect on suspended solids concentrations and other water quality constituents such as pH, hardness, and dissolved organic carbon (DOC). Suspended solids, for instance, affects metal partitioning. This in turn influences bioavailability and ultimately toxicity. Hence, it is critically important to consider flow in any water quality assessment. This can be especially important if the measured concentration of the metal is marginally greater than the magnitude component of the criterion. Within the context of the current chronic criterion assessment, we checked to determine whether flow was stable for the four-day period prior to grab sampling for metals. If flow was judged stable, then the measured concentration was considered representative of a four-day average. If flow was not stable, the result was judged to be not representative of a four-day average and therefore not suitable to be compared to chronic criteria. However, as noted above, the available data was already compared to the acute criteria, thus, all available data was considered in this assessment.

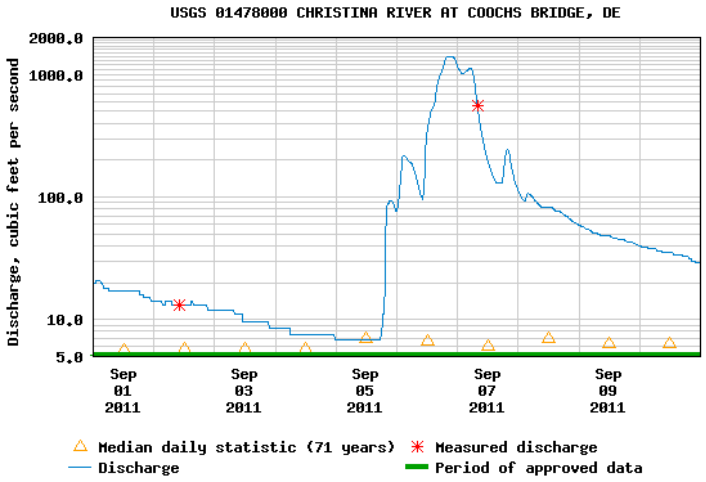
For each sample date in the table, stream flow conditions were assessed using USGS flow gauges in the same or nearby watersheds to see if the stream hydrograph was reasonably representative of a four day average flow period that describes the duration period of chronic criteria. Hydrographs appear below.

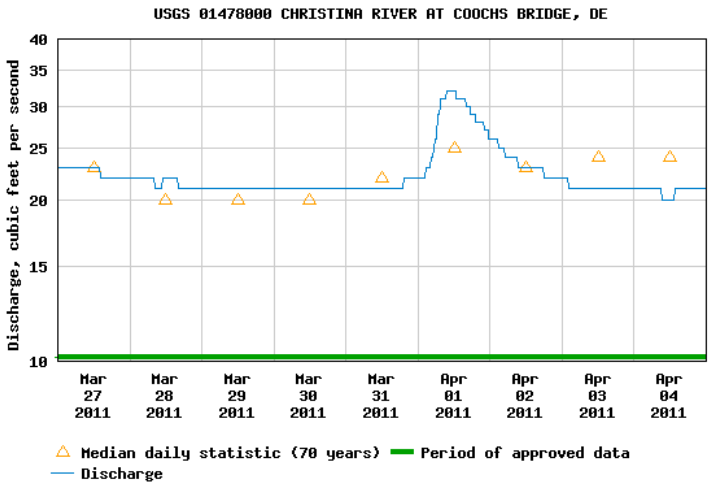
Table 3: Freshwater Sampling Events That May be Contributors to Standards Exceedances for Chronic Criteria

Station ID	date	Salinity	Fresh or Marine	Hardness	Copper (ug/l)	Zinc (ug/l)	Copper chronic criteria	Copper acute criteria	Zinc Chronic criteria	Zinc acute criteria	% Copper chronic criteria	% Copper acute criteria	%Zn Chrnoic Criteria	% Zn Acute Criteria
106141	5/18/2011	0.1	F	54.7	6.0	22.2	5.3	7.6	70.9	70.3	112.2%			
106141	9/8/2011	0.2	F	48.1	5.5		4.8	6.7	63.5	63.0	114.8%			
106141	4/2/2012	0.1	F	77.3	7.9	52.1	7.2	10.5	95.0	94.2	109.9%			
309041	5/28/2013	0.1	F	49.7	10.2		4.9	7.0	65.3	64.8	207.0%	146.7%		
309041	7/29/2013	0.1	F	49.1	5.6		4.9	6.9	64.7	64.1	114.8%			

Station 106141 is in the Christina River and co-located with USGS gauging station 01478000 at Coochs Bridge, DE. Flows on 5/18/2011, 9/9/2011 and 4/2/2012 are not representative of 4 day averages, thus no further assessment or listing action was required at the station.

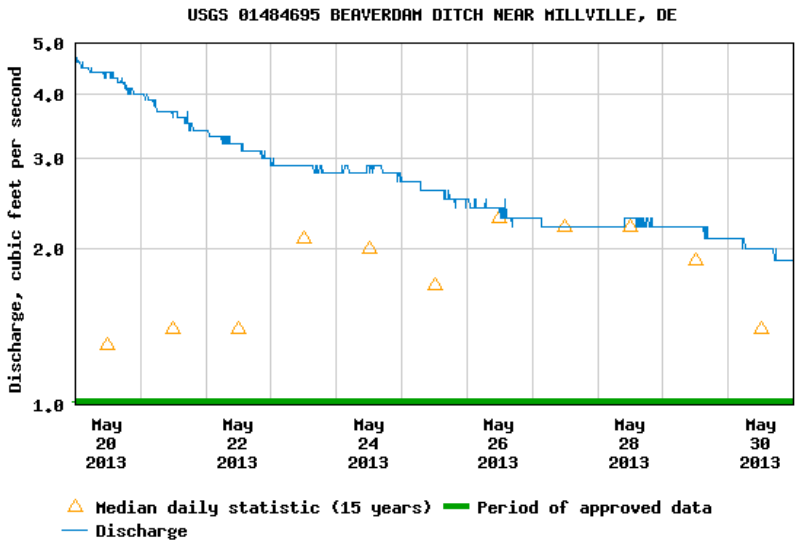


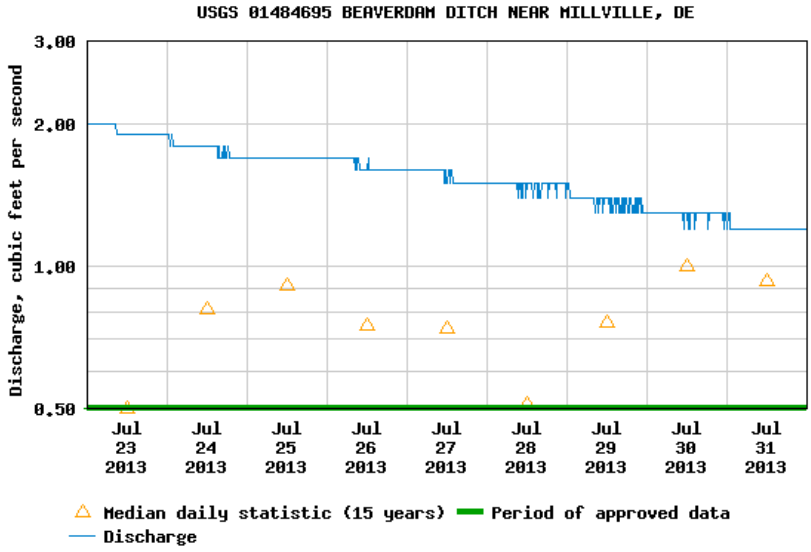




Station 309041 is in Wharton's Branch at Rt. 334 Bridge in the Iron Branch watershed. USGS 01484695 in the Beaverdam Ditch near Millville, DE was selected as the representative flow station.

Station 309041, Wharton's Branch, dates 5/28/2013 and 7/29/2013 are not representative of four day average flows and no further assessment or listing action was taken at this station.





Summary

3202 sample events for copper, lead and zinc at 80 sampling stations in fresh and marine waters from September 2008- August 2013 were evaluated for aquatic life use support determinations. As a result, 19 stations were assessed as not supporting the aquatic life use because of violations of acute water quality criteria for copper at 18 marine stations and zinc at a single fresh water station. All were placed on the Delaware 2014 Draft 303(d) list for public comment.