

**HAWK INLET MONITORING PROGRAM
2012 ANNUAL REPORT**



Hecla Greens Creek Mining Company

January 2013

TABLE OF CONTENTS

1.0 INTRODUCTION

- 1.1 Site Description**
- 1.2 Hawk Inlet Monitoring Program**
- 1.3 Deviation(s) from Program and Incidents in 2012**

2.0 WATER COLUMN MONITORING

- 2.1 2012 Analytical Results**
- 2.2 Data Evaluation**
- 2.3 QA/QC Results**

3.0 SEDIMENT MONITORING

- 3.1 2012 Analytical Results**
- 3.2 Data Evaluation**
- 3.3 QA/QC Results**

4.0 IN-SITU BIOASSAYS

- 4.1 2012 Analytical Results**
- 4.2 Data Evaluation**
- 4.3 QA/QC Results**

5.0 CONCLUSIONS

6.0 REFERENCES

TABLES

- 1-1 Summary of Permit Sampling Requirements
- 2-1 Hawk Inlet Water Column Field Parameters 2012
- 2-2 Hawk Inlet Water Column Monitoring Results 2012: Nonmetal Parameters
- 2-3 Hawk Inlet Water Column Monitoring Results 2012: Metals
- 2-4 Hawk Inlet Water Column Average Dissolved Metal Concentrations
- 3-1 Hawk Inlet Sediment Monitoring Field Parameters 2012
- 3-2 Hawk Inlet Sediment Results for Spring 2012
- 3-3 Hawk Inlet Sediment Results for Fall 2012
- 3-4 Hawk Inlet Sediment Data: Pre-Production Baseline, Production Period and Current Year Comparison
- 3-5 Average and Standard Deviation Values for Pre-Production, Production, and Current Year Sediment Data
- 3-6 Relative Standard Deviations (RSD) for Duplicate Sediment Samples

TABLES (continued)

- 4-1 Hawk Inlet Bioassay Monitoring Field Parameters 2012
- 4-2 Hawk Inlet Tissue Results for Spring 2012
- 4-3 Hawk Inlet Tissue Results for Fall 2012
- 4-4 Hawk Inlet Mussel Data: Pre-Production Baseline, Production Period and Current Year Comparison
- 4-5 Hawk Inlet *Nephtys* Data: Pre-Production Baseline, Production Period and Current Year Comparison
- 4-6 Average and Standard Deviation Values for Pre-Production, Production, and Current Year Mussel Data
- 4-7 Average and Standard Deviation Values for Pre-Production, Production, and Current Year *Nephtys* Data
- 4-8 Summary of Results for Additional Tissue Samples
- 4-9 Relative Standard Deviations (RSD) for Duplicate Tissue Samples

FIGURES (located at end of text)

- 1-1 Aerial Photo of Lower Hawk Inlet, Admiralty Island with Water, Sediment and Tissue Sampling Site Locations**
- 2-1a Sea Water pH Data: Site 106**
- 2-1b Sea Water pH Data: Site 107**
- 2-1c Sea Water pH Data: Site 108**
- 2-2a Sea Water EC Data: Site 106**
- 2-2b Sea Water EC Data: Site 107**
- 2-2c Sea Water EC Data: Site 108**
- 2-3a Sea Water Cadmium Data: Site 106**
- 2-3b Sea Water Cadmium Data: Site 107**
- 2-3c Sea Water Cadmium Data: Site 108**
- 2-4a Sea Water Copper Data: Site 106**
- 2-4b Sea Water Copper Data: Site 107**
- 2-4c Sea Water Copper Data: Site 108**
- 2-5a Sea Water Mercury Data: Site 106**
- 2-5b Sea Water Mercury Data: Site 107**
- 2-5c Sea Water Mercury Data: Site 108**
- 2-6a Sea Water Lead Data: Site 106**
- 2-6b Sea Water Lead Data: Site 107**
- 2-6c Sea Water Lead Data: Site 108**
- 2-7a Sea Water Zinc Data: Site 106**
- 2-7b Sea Water Zinc Data: Site 107**
- 2-7c Sea Water Zinc Data: Site 108**
- 3-1 Cadmium in Sediments Sites S-1, S-2**
- 3-2 Copper in Sediments Sites S-1, S-2**
- 3-3 Mercury in Sediments Sites S-1, S-2**
- 3-4 Lead in Sediments Sites S-1, S-2**
- 3-5 Zinc in Sediments Sites S-1, S-2**
- 3-6 Cadmium in Sediments Sites S-4, S-5S, S-5N**

FIGURES (continued)

- 3-7 Copper in Sediments Sites S-4, S-5S, S-5N**
- 3-8 Mercury in Sediments Sites S-4, S-5S, S-5N**
- 3-9 Lead in Sediments Sites S-4, S-5S, S-5N**
- 3-10 Zinc in Sediments Sites S-4, S-5S, S-5N**
- 4-1 Cadmium in Mussels STN-1, STN-2, STN-3 ESL**
- 4-2 Copper in Mussels STN-1, STN-2, STN-3 ESL**
- 4-3 Mercury in Mussels STN-1, STN-2, STN-3 ESL**
- 4-4 Lead in Mussels STN-1, STN-2, STN-3 ESL**
- 4-5 Zinc in Mussels STN-1, STN-2, STN-3 ESL**
- 4-6 Cadmium in *Nephtys* S-1, S-2, S-4**
- 4-7 Copper in *Nephtys* S-1, S-2, S-4**
- 4-8 Mercury in *Nephtys* S-1, S-2, S-4**
- 4-9 Lead in *Nephtys* S-1, S-2, S-4**
- 4-10 Zinc in *Nephtys* S-1, S-2, S-4**

APPENDIX

Appendix A Outfall Survey Footage CD

1.0 INTRODUCTION

1.1 Site Description

The Greens Creek Mine on Admiralty Island is located 18 miles southwest of the city of Juneau, Alaska. Dense forests cover the mountain slopes up to an elevation of 2500 feet, above which the vegetation is alpine. The climate is maritime, with precipitation similar to that in Juneau, averaging 60 to 70 inches per year at the mine site, and 45 to 55 inches per year at the facilities near Hawk Inlet. The mine and mill facilities (920 area) are located over 6 miles up Greens Creek from Hawk Inlet tidewater.

Zinc, lead, silver, and gold are the target recovery metals. The Greens Creek Mine operations began in August 1989, and operated approximately four years before production was suspended in April 1993. The mine and mill were recommissioned and operations restarted in mid-1996. A 2000 ton/day milling facility and appurtenant support facilities are in place at the 920 area. Filter pressed tailings from the milling process are backfilled in the mine and deposited in a surface dry-stack tailings pile near Hawk Inlet. Concentrate is transported from the mill to the Hawk Inlet area, where it is stored until it is shipped off-site.

Support facilities to the mining and milling operation at Hawk Inlet include core storage, concentrate storage and shipping, barge port facilities, and camp housing. A domestic waste water treatment plant is located at the Hawk Inlet port site.

Two waste water discharge outfalls and 10 storm water discharge sites are authorized by the HGCMC National Pollutant Discharge Elimination System (NPDES) Permit Number AK-004320-6. Outfall 001 provides an emergency backup discharge point for the Hawk Inlet Camp treated domestic sewage located at the Hawk Inlet port facilities. Under normal operating conditions, the Hawk Inlet camp treated sewage is combined with area surface runoff, and pumped up to the Tailings Area. Here it is combined with effluent streams from the 920 and the Tailings Basin areas, treated, and discharged through the submarine NPDES Outfall 002 onto the ocean floor in Hawk Inlet. Authority over the federal permitting, compliance and enforcement NPDES program transferred to the State (ADEC) in November of 2010 for the mining industry.

Hawk Inlet is a marine inlet formed during the late Holocene glaciation and is underlain by a series of late-Paleozoic to Mesozoic phyllitic-schist and greenstone formations. Hawk Inlet extends seven miles north from Chatham Strait to a tidal mudflat estuary about 0.6 miles in diameter. The narrow channel connecting the Inlet to Chatham Strait, located between the top of the Greens Creek delta and the western shore of Hawk Inlet, has a minimum low tide depth of 35 feet. The midchannel depth ranges from 35 feet to 250 feet. The Inlet has regular, twice-daily tides, with a maximum tidal variation of 25 feet. On the flood tide, the surface 35-foot layer contains the bulk of the water transport entering the Inlet and is then flushed out on the ebb tide. Flushing describes the rate and extent to which a body of water is replenished by tidal or other currents. Flushing rates are also indicative of the length of time that mining effluent may remain in a water body

and become incorporated into the physical and biological ecosystem through ingestion, adsorption or other means. In 1981, dispersion dye testing in Hawk Inlet determined that over each tidal cycle, an average of 13 billion gallons of water is flushed from the Inlet (SEA Associates, 1981). At that rate, it is estimated that the Inlet will completely flush at least once every five tidal cycles. Based on the mine output up through 1995, the input of effluent from the mining operations over this flushing period represents approximately 0.009 percent of the total flushing volume (Ridgeway, 2003).

For more in-depth information on the physical and biological characteristics of Hawk Inlet, see *Technical Review of the Status of Essential Fish Habitat in Hawk Inlet Subsequent to Mining Operations*, Ridgeway, October 2003.

1.2 Hawk Inlet Monitoring Program

In anticipation of the Greens Creek Mine development, government agencies, scientists and biological consultants carried out surveys of marine life and baseline studies of heavy metals in the environment beginning in the early 1980s. Several researchers have studied marine life in Hawk Inlet, and the on-going quarterly and semi-annual monitoring events have generated an extensive time-series data set of coincident metal levels in water, sediment, and marine tissue samples.

This *Hawk Inlet Monitoring Program 2012 Annual Report* has been prepared by Hecla Greens Creek Mining Company (HGCMC) in accordance with Section I.D.5 of the National Pollutant Discharge Elimination System (NPDES) Permit AK-004320-6. Authority over the federal permitting, compliance and enforcement NPDES program transferred to the State (ADEC) in November of 2010 for the mining industry. Reporting the Hawk Inlet monitoring program data in an annual report is a requirement of this permit, which became effective July 1, 2005. Prior to this, the data were reported to EPA and ADEC in quarterly seawater reports.

The primary objective of the Hawk Inlet monitoring program is to document the water quality, sediment and biological conditions in receiving waters and marine environments that may be impacted by the mine's operations. Sea water is sampled quarterly at three locations in Hawk Inlet, and sediment and invertebrate samples are taken each year in the spring and in the fall at four and seven locations, respectively. Figure 1-1 shows a site map with the sampling locations. Table 1-1 summarizes the requirements of the permit for sample parameters, sample preservation and holding time, sampling frequency, analytical methods and method required detection limits (MDLs). Specific quality assurance/quality control (QA/QC) requirements (i.e., sampling procedures, documentation, chain of custody processes, calibration procedures and frequency, data validation, corrective actions, etc.) are outlined in the NPDES Quality Assurance Plan: Project Monitoring Manual (HGCMC, 2009).

TABLE 1-1 Summary of Permit Sampling Requirements for Hawk Inlet

NPDES Requirement	Parameter	Required Sampling Frequency	Sample Type	Sample Container	Sample Preservation	Laboratory	Holding Time	Analytical Method(s)	Minimum Required Method Detection Limit	Units	Comments		
RECEIVING WATER COLUMN MONITORING													
I.D.1 Table 4	Dissolved Cadmium	Quarterly	Grab (1 sample for all metals)	1 ea. 500 ml Teflon bottle (1 bottle for all metals)	HNO ₃ to pH <2 by lab	Battelle Marine Sciences	6 months	EPA 213.2/ 1638	0.10	µg/L	MDLs set by NPDES permit Section I.D.1, Table 4		
I.D.1 Table 4	Dissolved Copper	Quarterly						EPA 220.2/ 1638	0.03	µg/L			
I.D.1 Table 4	Dissolved Lead	Quarterly						EPA 239.2/ 1638	0.05	µg/L			
I.D.1 Table 4	Total Mercury	Quarterly						28 days	EPA 245.1/ 1631	0.20		µg/L	
I.D.1 Table 4	Dissolved Zinc	Quarterly						6 months	EPA 289.2/ 1638	0.20		µg/L	
I.D.1 Table 4	Total Suspended Solids	Quarterly	Grab	1 ea. 1 liter plastic bottle	Cool to 4°C	Admiralty Environmental Labs	7 days	EPA 160.2/ SM 2540D	--	mg/L			
I.D.1 Table 4	Turbidity	Quarterly	Grab	1 ea. 1 liter plastic bottle	Cool to 4°C	Admiralty Environmental Labs	48 hours	EPA 180.1	--	NTU			
I.D.1 Table 4	WAD Cyanide	Quarterly	Grab	1 ea 1 liter plastic bottle	NaOH to pH >12, cool to 4°C	ACZ Labs	14 days	EPA 335.2/ SM 4500-CN-E	1.00	µg/L	Add 0.6g ascorbic acid, if chlorine is present.		
I.D.1 Table 4	pH	Quarterly	Grab	NA	NA	Field measurement	15 min	EPA 150.1/ SM 4500-H, B	--	SU			
I.D.1 Table 4	Conductivity	Quarterly	Grab	NA	NA	Field measurement	20 days	EPA 120.1	--	µmhos/cm			
I.D.1 Table 4	Temperature	Quarterly	Grab	NA	NA	Field measurement	15 min	NA	--	°C			
BIOACCUMULATION WATER SEDIMENT MONITORING													
I.D.2 Table 5	Total Cadmium	Semi-annual	Grab	2 ea. 8 oz. plastic or glass jar	Freeze sample	Columbia Analytical Services (CAS)		PSEP/GFAA	0.30	mg/Kg	MDLs set by NPDES permit Section I.D.2, Table 5		
I.D.2 Table 5	Total Copper	Semi-annual	Grab					CAS	PSEP/ICP	15.00		mg/Kg	
I.D.2 Table 5	Total Lead	Semi-annual	Grab					CAS	PSEP/ICP	0.50		mg/Kg	NMFS request duplicate sampling
I.D.2 Table 5	Total Mercury	Semi-annual	Grab					CAS	PSEP/ EPA 7471A	0.02		mg/Kg	
I.D.2 Table 5	Total Zinc	Semi-annual	Grab					CAS	PSEP/ICP	15.00		mg/Kg	
BIOACCUMULATION WATER IN-SITU BIOASSAY MONITORING													
I.D.3 Table 6	Total Cadmium	Semi-annual	Grab	2 ea. 8 oz. plastic or glass jar	Freeze sample	CAS		EPA 200.8/ 6020	not specified	mg/Kg	NMFS request duplicate sampling since Fall 2004		
I.D.3 Table 6	Total Copper	Semi-annual	Grab					CAS	EPA 200.8/ 6020	not specified		mg/Kg	
I.D.3 Table 6	Total Lead	Semi-annual	Grab					CAS	EPA 200.8/ 6020	not specified		mg/Kg	
I.D.3 Table 6	Total Mercury	Semi-annual	Grab					CAS	EPA 7471A	not specified		mg/Kg	
I.D.3 Table 6	Total Zinc	Semi-annual	Grab					CAS	EPA 200.8/ 6020	not specified		mg/Kg	

In May 2012, Marine Taxonomic Services surveyed the outfall pipeline for corrosion or damage. A CD of the survey footage can be found in Appendix A. The following points summarize the major findings of the inspection (Marine Taxonomic Services, 2012):

- In general, the outfall pipe was found to be in excellent overall condition.
- The outfall pipe showed no signs of degradation, cracking, and leakage and no restriction of diffuser ports.
- The minimal sediment accretion inside the pipe is characterized by elevated levels of metals but is not an immediate threat to discharge flow rates and requires no maintenance removal at the present time.

This report presents information on each of the three media sampled in Hawk Inlet: water column, sediment and in-situ bioassay. All results for the samples collected in 2012 are presented, along with the associated QA/QC data. Statistical evaluation of the data showing averages, variations, and changes over time are also included. The next section

describes any deviations from the monitoring program that occurred in 2012, and the reasons for the deviations.

1.3 Deviation(s) from Monitoring Program and Incidents in 2012

There were no deviations from the monitoring program in 2012.

There were no incidents that occurred in Hawk Inlet in 2012.

2.0 WATER COLUMN MONITORING

The receiving water column monitoring requirements originate from Section I.D.1 and Table 4 of the NPDES permit. The objective of the receiving water column monitoring element of the sampling program is to provide scientifically valid data on specific physical and chemical parameters for Hawk Inlet water quality. These data are used to evaluate potential changes in the Hawk Inlet marine environment.

Three ocean sites in Hawk Inlet are sampled to monitor potential water quality effects from the mine. Seawater samples are collected quarterly from the sites on an outgoing tide, with the Chatham Strait sample (Site 106) collected just after low slack water. The two other sites are Station 107, located about mid-way east-west in Hawk Inlet and west of the ship loader facility, and Station 108, located above the 002 diffuser in the mixing zone. Samples at all three locations are taken at a depth of five feet. Sample timing in each quarter is tide dependent, and is also weather dependent, as safety of the personnel conducting the sampling is a primary concern.

Water samples are sent to Battelle Marine Science Lab in Sequim, Washington, for low level dissolved trace metals analyses, ACZ Laboratory in Steamboat Springs, Colorado for WAD CN, Admiralty Environmental in Juneau, Alaska for pH, conductivity, total suspended solids, and turbidity analyses. Temperature, pH, turbidity and conductivity are measured in the field by the Environmental staff.

2.1 2012 Analytical Results

The tables in this section summarize the results for the quarterly water column monitoring conducted in 2012.

TABLE 2-1 Hawk Inlet Field Parameters 2012 (sample depth 5')

	Sample Date	Sample Time	Weather Conditions	Conductivity (µmhos/cm)	pH	Temp. (°C)
Site 106						
	3/12/12	10:46	partly sunny	15,130	8.02	3.3
	6/11/12	13:19	overcast	29,980	8.36	8.8
	8/6/12	10:55	cloudy	43,620	8.24	10.8
	10/17/12	09:10	cloudy	43,340	8.19	8.9
Site 107						
	3/12/12	10:29	partly sunny	16,990	8.01	3.2
	6/11/12	12:45	overcast	22,520	8.26	8.9
	8/6/12	10:15	rainy	42,640	8.12	11.2
	10/17/12	08:25	cloudy, overcast	41,580	8.20	8.8
Site 108						
	3/12/12	11:01	partly sunny	18,040	8.00	3.6
	6/11/12	13:02	overcast	27,130	8.30	9.2
	8/6/12	10:35	rainy	42,900	8.17	11.5
	10/17/12	08:50	cloudy, overcast	43,190	8.16	8.8

TABLE 2-2 Hawk Inlet Water Column Monitoring 2012: Nonmetal Parameters
(ACZ Laboratories and Admiralty Environmental) (sample depth 5')

	Sample Date	TSS (mg/L)	Turbidity (NTU)	WAD CN (µg/L)	pH (su)	Conductivity (µmhos/cm)
Site 106						
	3/12/12	11	0.18	<3.0	7.69	49,000
	6/11/12	19	1.74	<3.0	8.28	39,000
	8/6/12	20	0.5	<3.0	8.25	28,800
	10/17/12	26	<1	<3.0	8.06	19,700
Site 107						
	3/12/12	8	0.33	<3.0	7.74	49,500
	6/11/12	35	1.64	<3.0	8.21	37,700
	8/6/12	64	0.5	<3.0	8.18	35,000
	10/17/12	15	<1	<3.0	8.02	20,100
Site 108						
	3/12/12	14	0.18	<3.0	7.77	48,800
	6/11/12	20	2.21	<3.0	8.23	36,600
	8/6/12	96	0.5	<3.0	8.17	35,100
	10/17/12	27	<1	<3.0	8.09	20,200

TABLE 2-3 Hawk Inlet Water Column Monitoring Results 2012: Metals
(Battelle Marine Sciences Laboratory) (sample depth 5')

	Sample Date	Cd (µg/L) Dissolved	Cu (µg/L) Dissolved	Pb (µg/L) Dissolved	Hg (µg/L) Total	Zn (µg/L) Dissolved
	<i>Lab MDL</i>	(0.002)	(0.023)	(0.001)	(0.0001)	(0.042)
	<i>Req. MDL</i>	(0.10)	(0.03)	(0.05)	(0.0002)	(0.20)
Site 106						
	3/12/12	0.082	0.249	0.023	0.0004	1.40
	6/11/12	0.065	0.457	0.014	0.0004	1.11
	8/6/12	0.059	0.271	0.014	0.0003	0.552
	10/17/2012	0.073	0.321	0.019	0.0003	1.15
Site 107						
	3/12/12	0.085	0.320	0.074	0.0004	1.38
	6/11/12	0.069	0.991	0.025	0.0008	1.43
	8/6/12	0.059	0.688	0.049	0.0006	0.709
	10/17/2012	0.075	0.519	0.040	0.0006	1.10
Site 108						
	3/12/12	<0.002	<0.023	0.030	0.0004	0.565
	6/11/12	0.068	0.412	0.019	0.0005	1.61
	8/6/12	0.058	0.299	0.021	0.0008	0.890
	10/17/2012	0.077	0.353	0.028	0.0005	1.03

2.2 Data Evaluation

Figures 2-1a, b, c through 2-7a, b, c show the time series plots of field pH, conductivity, cadmium, copper, lead, mercury and zinc for Stations 106 (2-1a through 2-7a), 107 (2-1b through 2-7b) and 108 (2-1c through 2-7c). The Alaska Water Quality Standards (AWQS) for marine aquatic life – chronic levels, are shown or noted on the graphs where applicable. The graphs show that the HGCMC results remain within or below these standards in all historical and 2012 samples. The field conductivity at all 3 sites on 3/12/12 is unusually low; however, the lab conductivity is within the historical range. The lab conductivity at all 3 sites on 10/17/12 is unusually low; however, the field conductivity is within the historical range. It appears the field conductivity results on 3/12/12 and the lab conductivity results on 10/17/12 were reported at the sample temperature and not the standardized reporting temperature of 25 degrees Celsius.

The elevated WAD CN results for 2009 and 2010 are likely an artifact of instrumentation and other analytical difficulties at the laboratory rather than actual concentrations in the samples. Valley Environmental Laboratory purchased new instrumentation in 2009, updating their extraction apparatus and spectrophotometer. Potential issues with new instrumentation, along with the difficult matrix that these samples are in (ocean water), and the low detection limit that is required (<1 µg/L), can result in interferences that affect the results. An additional reason to question the validity of these results can be found in the WAD CN analyses of the HGCMC discharges to Hawk Inlet. In 2010, of the 52 samples of discharge water, 50 of the WAD CN results were < 3.0 µg/L. Because of these discrepancies, HGCMC collected additional duplicate WAD CN samples in 2010 and sent them to labs other than Valley to be analyzed. Duplicate samples for the 1st, 2nd and 4th quarters were sent to ACZ Laboratory, as well as to Analytica Laboratory for the 4th quarter samples. All duplicate samples from the two additional labs showed below detection limits of WAD CN (<3 and <1.2 µg/L, respectively). With the results of the WAD CN in the discharge water, as well as the duplicate sampling results, HGCMC decided that Valley Laboratory's results were suspect, and proposed to use ACZ Laboratory for future analysis of WAD CN samples. HGCMC sent all WAD CN samples in 2011 and 2012 to ACZ Laboratories and the results were all below the detection limit of <3 µg/L.

Table 2-4 summarizes the past five year's average metals values for the sea water samples, compared to the current year's results.

TABLE 2-4 Hawk Inlet Water Column Average Dissolved Metal Concentrations

	Cd (µg/L)		Cu (µg/L)		Pb (µg/L)		Hg (TOTAL - µg/L)		Zn (µg/L)	
	2007, 2008, 2009, 2010, and 2011	2012	2007, 2008, 2009, 2010, and 2011	2012	2007, 2008, 2009, 2010, and 2011	2012	2007, 2008, 2009, 2010, and 2011	2012	2007, 2008, 2009, 2010, and 2011	2012
Site 106	0.071	0.069	0.350	0.322	0.089	0.024	0.0005	0.0003	1.19	1.05
Site 107	0.074	0.072	0.500	0.630	0.090	0.047	0.0011	0.0006	1.46	1.15
Site 108	0.071	0.068	0.382	0.331	0.074	0.024	0.0010	0.0005	1.30	1.02

2.3 QA/QC Results

Battelle Marine Sciences Laboratory, ACZ Laboratories, and Admiralty Environmental analyzed the required parameters (see Table 1-1) in the sea water samples. Complete QA plans and reports are kept on file in each lab's office and are available upon request. The remainder of this section summarizes the relevant QA/QC results from each laboratory for the 2012 sea water samples (taken quarterly – 1Q12, 2Q12, 3Q12, and 4Q12). Elevated levels of zinc in the field blanks, often at levels higher than all the other sea water samples, have been noted consistently by Battelle for this sampling program. HGCMC is planning on working closely with Battelle in 2013 to determine the reason for this inconsistency.

Battelle Marine Science (low level dissolved trace metals analyses in salt water matrices):

1Q12: Target detection limits were met for all metals except copper and cadmium in one sample (site 108). Results for the method blank were less than the MDL for all metals. The field blank detected copper, mercury, zinc, and lead. The copper and mercury were detected at less than five times the MDL. Zinc and lead were detected well above the MDL and at high enough concentrations to impact field sample concentrations. Standard reference material (SRM) results were within the default criteria of $\pm 25\%$.

2Q12: Target detection limits were met for all metals. Method blank results were less than the MDL for all metals. The field blank detected zinc, lead, and mercury. Mercury was detected at less than two times the MDL. Zinc and lead were detected at well above the MDL and at concentrations high enough to impact field sample concentrations. Standard reference material (SRM) results were within the default criteria of $\pm 25\%$.

3Q12: Target detection limits were met for all metals. Method blank results were less than the MDL for all metals. The field blank detected zinc, lead, and mercury. Mercury was detected at less than two times the MDL. Zinc and lead were detected at well above the MDL and at concentrations high enough to impact field sample concentrations. Standard reference material (SRM), matrix spike and duplicate results were within the default criteria of $\pm 25\%$.

4Q12: Target detection limits were met for all metals. Detected levels were less than the MDL for all metals in the method blank. The field blank detected copper, zinc, lead, and mercury. Copper, lead, and mercury were detected at less than three times the MDL. Zinc was detected at well above the MDL and at concentrations high enough to impact field sample concentrations. Standard reference material (SRM), matrix spike and duplicate results were within the default criteria of $\pm 25\%$.

ACZ Laboratories (WAD cyanide analyses):

1Q12: The samples were received outside of the recommended temperature range of 0 to 6 degrees C. Method-specific preservation criteria cannot be met due to sample matrix.

2Q12: The samples were received outside of the recommended temperature range of 0 to 6 degrees C. Method-specified preservation criteria cannot be met due to sample matrix.

3Q12: Method-specified preservation criteria cannot be met due to sample matrix.

4Q12: The samples were received outside of the recommended temperature range of 0 to 6 degrees C. Method-specified preservation criteria cannot be met due to sample matrix.

Admiralty Environmental (total suspended solids (TSS), pH, conductivity, and turbidity analyses):

1Q12, 2Q12, 3Q12, 4Q12: All method specifications and required MDLs were met.

3.0 SEDIMENT MONITORING

The requirements for the sediment monitoring originate from Section I.D.2, Sediment Monitoring, and Table 5 of the NPDES permit. The objective of this element of the monitoring program is to provide scientifically valid data on five specific trace metal parameters from sediments at four locations in Hawk Inlet. These data are used to evaluate potential changes in the Hawk Inlet marine environment.

The sediment samples are collected semi-annually in the spring and fall at the Greens Creek delta (Site S-1), Pile Driver Cove near the mouth of the inlet (Site S-2), near the ore dock (Site S-4), and under the ship's berth near the old cannery (Site S-5N and S-5S which bracket the area where concentrate was spilled in 1989). The samples are analyzed at Columbia Analytical Services, Inc. in Kelso, Washington for total concentrations of five trace metals (Cd, Cu, Pb, Hg, and Zn).

An additional location, Site S-3, has also been sampled for sediments since the 1980s. Site S-3 is located at the head of Hawk Inlet. Data collected from Site S-3 exhibited different trends from the other two background stations (S-1 and S-2). Most metals at S-3 were found at higher levels than at S-1 or S-2. Field observations of a mass wasting event in the watershed above S-3 appears to have released metals from abandoned historic mine workings (Alaska Rand Group) into the environment (Ridgeway, 2003). For this reason, when the reissued permit became effective July 1, 2005, S-3 was dropped from the list of active sediment sampling sites. Therefore, data from S-3 are not presented in this report.

3.1 2012 Analytical Results

All sediment samples were collected by Marine Taxonomic Services, LTD. The sample locations, dates, times, weather conditions, and tides are shown in Table 3-1. Tables 3-2 and 3-3 in this section summarize the total metals results for the semi-annual sediment monitoring events. Sample labels I, II, and III denote duplicate samples taken at each sample site.

TABLE 3-1 Hawk Inlet Sediment Monitoring Field Parameters 2012

Locations	Date Sampled	Time Sampled	Weather Conditions	Tide Ht.
S-1	5/5/12	6:00	overcast	0.1
	8/29/12	5:30	overcast	0.5
S-2	5/5/12	7:45	overcast	0.3
	8/29/12	5:00	overcast	0.7
S-4	5/7/12	7:50	rain	0.2
	8/29/12	6:45	overcast	0.1
S-5S	5/8/12	14:30	overcast	8.4
	8/30/12	14:00	rain	9.4
S-5N	5/8/12	15:30	overcast	9.1
	8/30/12	15:00	rain	9.0

TABLE 3-2 Hawk Inlet Sediment Results for Spring 2012
(Columbia Analytical Services Laboratory)

Sample No.	Sample date	Cd (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	Hg (mg/kg dw)	Zn (mg/kg dw)
<i>Lab MRL</i>		(0.01, 0.02)	(0.06, 0.07, 0.08, 0.09)	(0.04, 0.05, 0.29)	(0.01, 0.02)	(0.35, 0.36, 0.37, 0.38, 0.39, 0.40, 0.45, 0.46, 2.87)
<i>Required MDL</i>		(0.3)	(15.0)	(0.05)	(0.02)	(15.0)
S-1 Sediments-Metals I	5/5/12	0.13	13.2	6.70	0.03	101
S-1 Sediments-Metals II	5/5/12	0.13	13.0	6.01	0.02	96.8
S-1 Sediments-Metals III	5/5/12	0.14	15.5	7.40	0.03	121
S-2 Sediments-Metals I	5/5/12	0.13	7.40	1.53	<0.01	36.8
S-2 Sediments-Metals II	5/5/12	0.14	7.40	1.62	<0.01	35.1
S-2 Sediments-Metals III	5/5/12	0.16	9.30	1.70	<0.01	42.0
S-4 Sediments-Metals I	5/7/12	0.26	17.1	18.2	0.03	58.4
S-4 Sediments-Metals II	5/7/12	0.26	17.9	20.0	0.03	58.7
S-4 Sediments-Metals III	5/7/12	0.26	16.5	22.6	0.03	60.8
S-5N Sediments-Metals I	5/8/12	1.05	40.1	145	0.19	179
S-5N Sediments-Metals II	5/8/12	1.37	74.0	725	0.11	233
S-5N Sediments-Metals III	5/8/12	1.70	67.3	296	0.11	294
S-5S Sediments-Metals I	5/8/12	0.99	141	428	0.11	218
S-5S Sediments-Metals II	5/8/12	1.35	121	233	0.19	332
S-5S Sediments-Metals III	5/8/12	1.36	238	1900	0.37	317

TABLE 3-3 Hawk Inlet Sediment Results for Fall 2012
(Columbia Analytical Services Laboratory)

Sample No.	Sample date	Cd (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	Hg (mg/kg dw)	Zn (mg/kg dw)
<i>Lab MRL</i>		(0.01, 0.02)	(0.10)	(0.02, 0.03, 0.04, 0.54, 0.65, 0.66)	(0.02, 0.10)	(0.20, 0.30, 0.40, 5.40, 6.50, 6.60)
<i>Required MDL</i>		(0.3)	(15.0)	(0.05)	(0.02)	(15.0)
S-1 Sediments-Metals I	8/29/12	0.07	9.1	5.30	0.02	53.5
S-1 Sediments-Metals II	8/29/12	0.11	8.4	5.28	0.03	58.3
S-1 Sediments-Metals III	8/29/12	0.10	9.6	4.76	0.03	63.6
S-2 Sediments-Metals I	8/29/12	0.08	6.0	2.03	<0.02	31.4
S-2 Sediments-Metals II	8/29/12	0.09	6.1	1.87	<0.02	30.4
S-2 Sediments-Metals III	8/29/12	0.10	6.0	1.72	<0.02	29.4
S-4 Sediments-Metals I	8/29/12	0.07	9.7	16.4	0.02	37.0
S-4 Sediments-Metals II	8/29/12	0.07	13.2	13.8	0.03	35.8
S-4 Sediments-Metals III	8/29/12	0.07	8.2	15.1	<0.02	34.3
S-5N Sediments-Metals I	8/30/12	1.25	24.8	82	0.11	156
S-5N Sediments-Metals II	8/30/12	1.18	27.3	97	0.18	176
S-5N Sediments-Metals III	8/30/12	1.44	99.6	246	0.15	567
S-5S Sediments-Metals I	8/30/12	2.13	47.8	1950	0.29	543
S-5S Sediments-Metals II	8/30/12	6.68	60.8	391	1.10	1270
S-5S Sediments-Metals III	8/30/12	5.20	79.3	309	0.34	1020

3.2 Data Evaluation

Prior to opening the Greens Creek mine for full production in August 1989, sediment and biota tissues were sampled for heavy metal concentrations. Sampling sites S-1 and S-2 were chosen to represent natural conditions; therefore, results from these sites from June of 1984 until August of 1989 were used to calculate baseline, pre-production values. These data are useful as baseline values against which to compare metal values after mining began (Table 3-4), and the results for the current year's sampling. Sampling sites S-4 and S-5 are thought to have been influenced by the old cannery operation and mine exploration work and are not suitable for background calculations.

TABLE 3-4 Hawk Inlet Sediment Data: Pre-Production Baseline, Production Period and Current Year Comparison

Metal	Pre-Production (6/1984-8/1989)			Production (9/1989-9/2011)			Current Year 2012		
	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
Cd	0.24	0.03	0.87	0.20	0.06	0.89	0.10	0.07	0.13
Cu	18.7	11.9	33.0	14.6	7.50	39.5	8.94	6.00	13.2
Pb	6.72	2.20	13.0	5.65	<0.02	23.7	3.89	1.53	6.70
Hg	0.035	0.002	0.094	0.020	0.020	0.140	0.025	0.020	0.030
Zn	96.1	52.8	155	74.7	26.1	185	55.7	31.4	101

NOTE: Data are compilation of results from Stations S-1 and S-2; underlined average values higher than baseline

The comparison of pre-production and production sediment metal values in Table 3-4 shows that across Stations S-1 and S-2, the average metal levels are lower during the production/mining period than they were during pre-production. The current year's results show the average metals levels to be below the production period's average values for all metals except mercury. However, it is notable that all of the 2006 average metals concentrations were greater than the average production values (KGCMC, 2007). Based on these data, it appears that heavy metals in sediment continue to vary from year to year, and have not increased above the range of area-wide baseline levels during mining years.

Figures 3-1 through 3-5 show the time series plots for cadmium, copper, lead, mercury and zinc for sampling sites S-1 and S-2. Linear regression analyses on the data plots indicate that all five metal's concentration have not increased with time.

Sampling sites S-4 and S-5S and S-5N are located near the ore concentrate loading facility. In 1989, the first attempt to load a barge with ore concentrate resulted in a spill of concentrate into Hawk Inlet. A suction dredge company was brought on-site in 1995 to dredge the available concentrate off of the ocean floor. This effort was confounded somewhat by the residual debris from the 1974 cannery facility fire. Although clean-up

efforts were extensive, liter-sized pockets of concentrate are still observed throughout the area. Prop wash from ore ships and associated tug boats continues to both re-suspend these pockets and also mix them with natural sediments.

After the 1995 clean-up, the sampling methodology at S-5 was expanded. The site was sub-divided into two separate locations: adding site S-5S located on the south side of the spill area, to complement S-5N located on the north side. Following the spill, metal concentrations in the sediment in this area have been elevated and variable. The lead concentration at site S-5S for one of the 2012 samples showed an elevated concentration of 1,950 mg/kg. The duplicate samples at S-5S showed lead concentrations of 391 mg/kg and 309 mg/kg, which are within the historical range. Figures 3-6 through 3-10 show the metal time series graphs for sites S-4, S-5S, and S-5N.

HGCMC met with the USACE, ADEC, EPA, NOAA, USF&WS and Fish and Game in August 2012 to discuss potential dredging of sediments near the shiploader. The agencies will require intensive and plan-specific sampling of the sediments in the area, to be conducted under multiple agency reviews. This would all need to be completed prior to submitting a USACE permit application for removing any material.

Table 3-5 shows the average metal concentrations and the associated standard deviations for each sediment sampling site during pre-production, production, and the current year. Pre-production sediment metals average values show some consistency across stations, but the standard deviations for these data indicate high variability, representative of typical natural distributions.

TABLE 3-5 Average and Standard Deviation Values for Pre-Production, Production, and Current Year Sediment Data

Metal (mg/kg dw)	S-1					S-2				
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg	avg	stdev	avg	stdev	avg
Cd	0.25	0.22	0.24	0.18	0.10	0.24	0.12	0.17	0.08	0.11
Cu	22.50	5.19	17.50	7.12	11.15	15.01	2.68	11.75	4.11	6.72
Pb	8.18	2.63	<u>8.56</u>	4.43	6.00	5.26	2.16	2.73	1.74	1.78
Hg	0.04	0.02	0.03	0.03	0.03	0.03	0.01	0.01	0.02	<0.02
Zn	129.2	11.6	102.4	30.1	77.3	62.9	6.7	46.9	15.8	34.1

Metal (mg/kg dw)	S-4					S-5N			S-5S		
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012	post spill (9/1989 - 9/2011)		Current Year 2012	post spill (6/1995 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg	avg	stdev	avg	avg	stdev	avg
Cd	0.76	1.10	<u>0.87</u>	0.89	0.16	12.30	39.62	1.15	3.80	3.66	1.56
Cu	49.04	19.25	<u>52.98</u>	55.72	13.40	244.47	380.54	32.45	89.85	51.29	<u>94.40</u>
Pb	108.19	136.84	<u>111.02</u>	135.37	17.30	985	2328	113	257	192	<u>1189</u>
Hg	0.12	0.08	<u>0.20</u>	0.59	0.03	1.92	5.52	0.15	0.37	0.30	0.20
Zn	179.2	125.5	<u>180.1</u>	183.9	47.7	1992	5409	168	796	745	381

Note: Underlined averages are higher than pre-production averages

3.3 QA/QC Results

Columbia Analytical Services analyzed the required parameters (see Table 1-1) in the sediment samples. Complete QA plans and reports are kept on file in the lab's office and are available upon request. The remainder of this section summarizes any relevant QA/QC results that were exceptions for the spring and fall sampling events in 2012.

Spring 2012:

The Relative Percent Difference (RPD) for the replicate analysis of mercury in the Batch QCI sample was outside the normal CAS control limits. The variability in the results was attributed to the heterogeneous distribution of mercury in the sample. The samples were homogenized, freeze dried, and then ground prior to digestion; however this was not sufficient to achieve a completely uniform distribution of this analyte in the tissue.

Fall 2012:

The matrix spike recovery for copper for sample S-1 Sed Metals Rep I was outside control criteria. Recovery in the Laboratory Control Sample (LCS) was acceptable, which indicated the analytical batch was in control. The matrix spike outlier suggested a potential low bias in this matrix. No further corrective action was appropriate.

Beginning in the fall of 2004, duplicate samples have been collected from each site, where possible, to address a National Marine Fisheries Service request. Precision can be calculated from the results of duplicate samples. In this case, the relative standard deviation RSD (the standard deviation relative to the mean, expressed as a percent) is shown for the duplicate samples from 2012 in Table 3-6.

TABLE 3-6 RSDs for Duplicate Sediment Samples

SAMPLE ID	DATE	Cd	Cu	Pb	Hg	Zn
		(mg/kg dw)				
	DL	0.05	0.1	0.05	0.02	0.5
S-1 Sediments-Metals I	5/5/12	0.13	13.2	6.70	0.03	101
S-1 Sediments-Metals II	5/5/12	0.13	13.0	6.07	0.02	96.8
S-1 Sediments-Metals III	5/5/12	0.14	14.5	7.40	0.03	121
RSD		--	6.0	9.9	--	12.2
S-2 Sediments-Metals I	5/5/12	0.13	7.4	1.53	<0.01	36.8
S-2 Sediments-Metals II	5/5/12	0.14	7.4	1.62	<0.01	35.1
S-2 Sediments-Metals III	5/5/12	0.16	9.3	1.70	<0.01	42.0
RSD		--	13.6	5.26	--	9.5
S-4 Sediments-Metals I	5/7/12	0.26	17.1	18.2	0.03	58.4
S-4 Sediments-Metals II	5/7/12	0.26	17.9	20.0	0.03	58.7
S-4 Sediments-Metals III	5/7/12	0.26	16.5	22.6	0.03	60.8
RSD		1.35	4.1	10.9	--	2.2
S-5N Sediments-Metals I	5/8/12	1.05	40.1	145	0.19	179
S-5N Sediments-Metals II	5/8/12	1.37	74.0	725	0.11	233
S-5N Sediments-Metals III	5/8/12	1.70	67.3	296	0.11	294
RSD		23.7	29.7	77.4	33.8	24.4
S-5S Sediments-Metals I	5/8/12	0.99	141	428	0.11	218
S-5S Sediments-Metals II	5/8/12	1.35	121	233	0.19	332
S-5S Sediments-Metals III	5/8/12	1.36	238	1900	0.37	317
RSD		17.1	37.5	107	59.6	21.4

SAMPLE ID	DATE	Cd	Cu	Pb	Hg	Zn
		(mg/kg dw)	(mg/kg dw)	(mg/kg dw)	(mg/kg dw)	(mg/kg dw)
	DL	0.05	0.1	0.05	0.02	0.5
S-1 Sediments-Metals I	8/29/12	0.07	9.1	5.30	0.02	53.5
S-1 Sediments-Metals II	8/29/12	0.11	8.4	5.28	0.03	58.3
S-1 Sediments-Metals III	8/29/12	0.10	9.6	4.76	0.03	63.6
RSD		--	6.7	5.99	--	8.6
S-2 Sediments-Metals I	8/29/12	0.08	6.0	2.03	<0.02	31.4
S-2 Sediments-Metals II	8/29/12	0.09	6.1	1.87	<0.02	29.4
S-2 Sediments-Metals III	8/29/12	0.10	6.0	1.72	<0.02	29.4
RSD		--	1.0	8.28	--	3.3
S-4 Sediments-Metals I	8/29/12	0.07	9.7	16.4	0.02	37.0
S-4 Sediments-Metals II	8/29/12	0.07	13.2	13.8	0.03	35.8
S-4 Sediments-Metals III	8/29/12	0.07	8.2	15.1	<0.02	34.3
RSD		--	24.8	8.6	--	3.8
S-5N Sediments-Metals I	8/30/12	0.13	24.8	81.7	.011	156
S-5N Sediments-Metals II	8/30/12	1.18	27.3	96.7	0.18	176
S-5N Sediments-Metals III	8/30/12	1.44	99.6	246	0.15	567
RSD		--	84.0	64.2	24	77
S-5S Sediments-Metals I	8/30/12	2.13	47.8	1950	0.29	543
S-5S Sediments-Metals II	8/30/12	6.68	60.8	391	1.10	1270
S-5S Sediments-Metals III	8/30/12	5.20	79.3	309	0.34	1020
RSD		49.7	25.3	105	79	39

-- indicates RSD was not calculated because one or more of the values was less than 4 times the DL

The data quality objectives for the RSD are less than or equal to 30 percent, when the values are at least four times the detection limit. Twelve out of the 38 (approximately 32 percent) RSDs calculated for the 2012 duplicate samples were not within this data quality objective. All of the twelve samples that were out of the required limits were from sample sites S-5S and S-5N which are the sites that surround the area near the shiploader where a concentrate spill occurred in 1989. Due to the isolated pockets of concentrate remaining from the clean-up effort in 1995, sampling at these sites continues to show the greatest variability with associated higher RSDs typical of mixed population samples.

4.0 IN-SITU BIOASSAYS

The requirements for the bioassay monitoring originate from Section I.D.3, In-situ Bioassays, and Table 5 of the NPDES permit. The objective of this element of the monitoring program is to provide scientifically valid data on five specific trace metal parameters from the tissues of polychaete worms (*Nephtys*) and mussels at seven locations in Hawk Inlet. These data are used to evaluate potential changes in the Hawk Inlet marine environment.

Bioaccumulation in-situ bioassay sampling in Hawk Inlet consists of semi-annual testing of trace metal tissue burdens of selected species of invertebrate organisms with different feeding guilds. In the Hawk Inlet sill area, where no fine grained sediments occur, four sites (Stations STN-1, STN-2, STN-3 and East Shoal Light (ESL)) are used for in-situ bioassay monitoring of trace metals in bay mussels (*Mytilus edulis*). Data gathered from this area measures the response in organisms in the immediate vicinity of the process effluent discharge. In most other areas of Hawk Inlet, the bottom is covered with sediment. Consequently, samples of sediment dwelling polychaete worms (*Nephtys procera*), and when available sediment dwelling bivalves (*Cockles* and *Littleneck Clams*) are collected at three additional sites (S-1, S-2, and S-4).

An additional location, Site S-3, has also been sampled for biota since the 1980s. Site S-3 is located at the head of Hawk Inlet. Field observations of a mass wasting event in the watershed above S-3 appears to have released metals from abandoned historic mine workings (Alaska Rand Group) into the environment (Ridgeway, 2003). For this reason, when the reissued permit became effective July 1, 2005, S-3 was dropped from the list of active bioassay sampling sites. Therefore, data from S-3 are not presented in this report.

4.1 2012 Analytical Results

All tissue samples were collected by Marine Taxonomic Services, LTD. The sample locations, types, dates, times, weather conditions, and tides are shown in Table 4-1. Tables 4-2 and 4-3 in this section summarize the total metals results for the semi-annual bioassays. Sample labels I, II, and III denote duplicate samples taken at each site. Duplicate samples are not taken for all species due to the negative impact such removal would have on the relatively sparse populations present on the Hawk Inlet bioassay monitoring sample sites.

TABLE 4-1 Hawk Inlet Tissue Sampling Field Data 2012

Locations	Sample Type	Date Sampled	Time Sampled	Weather Conditions	Tide Ht.
S-1	Nepthys	5/5/12	6:45	overcast	-0.7
	Cockle	5/5/12	7:10	overcast	-0.7
S-2	Nepthys	8/29/12	6:15	overcast	-0.3
	Cockle	8/29/12	6:30	overcast	-0.1
	Nepthys	5/5/12	8:35	overcast	0.5
	Cockle	5/5/12	8:45	overcast	-0.7
	Littleneck	5/5/12	9:10	overcast	1.2
	Nepthys	8/29/12	18:00	overcast	0.4
S-4	Cockle	8/29/12	18:15	overcast	0.3
	Littleneck	8/29/12	18:40	overcast	0.2
	Nepthys	5/7/12	8:20	rain	-0.6
	Cockle	5/7/12	8:50	rain	-0.8
STN-1	Nepthys	8/28/12	17:35	clear	0.8
	Cockle	8/28/12	17:50	clear	0.8
STN-2	Mussels	5/11/12	12:00	clear	0.0
	Mussels	8/27/12	4:15	rain	0.3
STN-3	Mussels	5/11/12	14:00	clear	1.2
	Mussels	8/30/12	19:15	rain	0.0
ESL	Mussels	5/11/12	11:00	clear	1.0
	Mussels	8/27/12	5:00	rain	0.3
ESL	Mussels	5/11/12	10:00	clear	1.0
	Mussels	8/27/12	5:00	rain	0.6

TABLE 4-2 Hawk Inlet Tissue Results for Spring 2012
(Columbia Analytical Services Laboratory)

Sample No.	Sample date	Cd (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	Hg (mg/kg dw)	Zn (mg/kg dw)
BIOASSAYS						
<i>Lab MRL</i>		(0.02)	(0.1)	(0.02)	(0.02, 0.03)	(0.5)
S-1 NepthysI	5/5/12	2.47	5.4	0.44	0.03	178
S-1 NepthysII	5/5/12	2.33	6.8	0.47	0.03	211
S-1 NepthysIII	5/5/12	2.37	7.4	0.52	0.04	198
S-1 Cockles	5/5/12	1.16	4.0	0.63	0.02	91.3
S-2 NepthysI	5/5/12	0.91	5.6	0.53	<0.02	185
S-2 NepthysII	5/5/12	0.99	6.1	0.48	0.02	181
S-2 NepthysIII	5/5/12	0.91	6.7	0.51	0.02	188
S-2 Cockles	5/5/12	1.15	3.0	0.27	0.04	70.4
S-2 Littlenecks	5/5/12	2.80	7.0	0.26	0.03	97.9
S-4 NepthysI	5/7/12	0.39	6.0	3.76	<0.03	175
S-4 NepthysII	5/7/12	0.32	3.9	3.71	<0.02	175
S-4 NepthysIII	5/7/12	0.42	4.9	3.93	0.02	183
S-4 Cockles	5/7/12	0.87	4.6	3.37	0.02	92.8
STN-1 Mussels	5/11/12	10.4	6.4	0.80	0.04	94.2
STN-2 Mussels	5/11/12	9.05	6.3	0.48	0.03	94.3
STN-3 Mussels	5/11/12	10.8	6.2	0.74	0.04	93.4
ESL Mussels	5/11/12	9.83	7.6	0.68	0.02	99.6

TABLE 4-3 Hawk Inlet Tissue Results for Fall 2012
(Columbia Analytical Services Laboratory)

Sample No.	Sample date	Cd (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	Hg (mg/kg dw)	Zn (mg/kg dw)
BIOASSAYS						
<i>Lab MRL</i>		(0.02)	(0.1)	(0.02)	(0.02)	(0.5)
S-1 NephthysI	8/29/12	4.07	5.5	0.44	0.07	256
S-1 NephthysII	8/29/12	3.64	5.3	0.39	0.09	253
S-1 NephthysIII	8/29/12	3.34	5.9	0.37	0.06	206
S-1 Cockles	8/29/12	0.79	3.1	0.69	0.04	63.4
S-2 NephthysI	8/29/12	1.02	5.0	0.48	<0.02	193
S-2 NephthysII	8/29/12	0.94	6.7	0.50	<0.02	198
S-2 NephthysIII	8/29/12	0.87	5.6	0.48	<0.02	192
S-2 Cockles	8/29/12	0.73	3.4	0.65	0.04	55.1
S-2 Littlenecks	8/29/12	3.02	7.1	0.18	0.03	86.4
S-4 NephthysI	8/28/12	1.56	35.7	4.34	0.07	223
S-4 NephthysII	8/28/12	1.25	19.8	5.20	0.03	215
S-4 NephthysIII	8/28/12	1.03	16.7	5.03	0.03	206
S-4 Cockles	8/28/12	0.54	3.3	3.04	0.04	79.6
STN-1 Mussels	8/27/12	8.87	5.6	0.49	0.04	83.6
STN-2 Mussels	8/30/12	10.6	5.5	0.47	0.03	84.8
STN-3 Mussels	8/27/12	9.37	5.5	0.44	0.03	80.8
ESL Mussels	8/27/12	6.55	7.1	0.63	0.03	80.6

4.2 Data Evaluation

Prior to opening the Greens Creek mine for full production in August 1989, sediment and biota tissues were sampled for heavy metal concentrations. Results for mussels from sites STN-1, STN-2, STN-3 and ESL, and for *Nephthys* from sites S-1 and S-2 from June of 1984 until August of 1989 were used to calculate baseline, pre-production values. These data are useful as baseline values against which to compare metal values after mining began and the results for the current year's sampling (Table 4-4 and 4-5).

As noted by Oceanographic Institute of Oregon in the 1998 Kennecott Greens Creek Mine Risk Assessment (p 4-3),

“Sampling stations were selected to demonstrate a range of potential exposures including “worst case” exposure to Outfall discharges. Some of the test organisms placed in cages directly on the Outfall diffuser ports lived for six months. These results indicate that even maximum exposure to the Outfall discharge result in no acute effects.”

TABLE 4-4 Hawk Inlet Mussels Tissue Data: Pre-Production Baseline, Production Period and Current Year Comparison

Metal	Pre-Production (6/1984-8/1989)			Production (9/1989-9/2011)			Current Year 2012		
	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
Cd	7.67	3.25	15.8	<u>7.91</u>	<0.5	14.5	<u>9.43</u>	6.55	10.8
Cu	8.51	5.50	21.1	<u>8.52</u>	1.30	110	6.28	5.50	7.60
Pb	0.57	0.15	1.73	<u>2.65</u>	<0.2	92.5	<u>0.59</u>	0.44	0.80
Hg	0.064	0.014	0.560	0.036	<0.2	0.070	0.033	0.020	0.040
Zn	88.4	65.0	142	84.8	49.0	126	<u>88.9</u>	80.6	99.6

Data are compilation of results from Stations ESL, STN-1, STN-2 and STN-3

Average lead concentrations in mussel tissues are currently approximately five times higher during the production period than the pre-production period. Average lead values in 2012 were slightly higher than the pre-production, but lower than the production average values. Average zinc values in 2012 (88.9 mg/kg) were similar to pre-production values (88.4 mg/kg), and higher than production values (84.8 mg/kg).

When compared to the Mussel Watch averages for Alaska, cadmium and zinc exceeded these averages (2.87 mg/kg and 87.95 mg/kg, respectively) during pre-production. Cadmium and lead exceeded these averages (2.87 mg/kg and 1.17 mg/kg, respectively) during production. These levels were similarly noted in the 2003 Review of the Status of Essential Fish Habitat in Hawk Inlet Subsequent to Mining Operations (p 57):

“...the average mining production period metal levels are generally below Mussel Watch averages for Alaska. The exception to this is Cd, which was above Mussel Watch Alaska averages prior to and subsequent to mining operations. Because the USFWS Hawk Inlet-wide levels of Pb increased similarly to the outfall monitoring site levels of Pb, these increases over time may be due to natural increases in Pb in the environment.”

TABLE 4-5 Hawk Inlet *Nephtys* Tissue Data: Pre-Production Baseline, Production Period and Current Year Comparison

Metal	Pre-Production (6/1984-8/1989)			Production (9/1989-9/2011)			Current Year 2012		
	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
Cd	2.65	0.24	6.91	2.03	0.28	4.97	2.12	0.91	4.07
Cu	10.2	6.24	17.4	10.0	4.30	42.1	5.38	5.00	5.60
Pb	0.48	0.13	1.07	<u>0.97</u>	<0.02	4.76	0.47	0.44	0.53
Hg	0.03	0.01	0.07	<u>0.05</u>	<0.02	1.67	0.03	<0.02	0.07
Zn	206	121	303	188	62.6	357	203	178	256

Data are compilation of results from Stations S-1 and S-2

Average lead and mercury concentrations in the indicator polychaete worm, *Nephtys*, are currently higher in the production years than pre-production values. However, all average metals concentrations were similar or lower in 2012 than in the pre-production years. All metals concentrations will continue to be monitored.

Tables 4-6 and 4-7 show the average and standard deviation results for pre-production and production periods for the individual sites for mussels and *Nephtys*, respectively. Table 4-6 shows larger standard deviations in production levels of lead and copper concentrations in mussels at all sites. Also, copper shows a large increase in standard deviation for the ESL site during production sampling. This is thought to be due to a single extreme and potentially anomalous value of 110 mg/kg dw from 1992. Table 4-7 shows larger standard deviations in production levels of lead concentrations in *Nephtys* at S-1, S-2 and S-4.

TABLE 4-6 Average and Standard Deviation Values for Pre-Production, Production, and Current Year Mussel Data

Metal (mg/kg dw)	ESL					STN-1				
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg	avg	stdev	avg	stdev	avg
Cd	6.17	1.78	<u>6.69</u>	1.67	<u>8.19</u>	7.48	1.72	<u>7.85</u>	1.84	<u>9.64</u>
Cu	9.61	3.77	<u>11.11</u>	16.27	7.35	8.05	1.19	7.42	1.76	6.00
Pb	0.53	0.26	<u>1.37</u>	0.77	<u>0.66</u>	0.66	0.44	<u>1.36</u>	0.86	0.65
Hg	0.03	0.01	<u>0.04</u>	0.08	0.03	0.10	0.14	0.04	0.02	<u>0.65</u>
Zn	90.2	8.1	82.9	14.7	90.1	88.5	15.4	84.4	14.4	<u>88.9</u>

Metal (mg/kg dw)	STN-2					STN-3				
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg	avg	stdev	avg	stdev	avg
Cd	8.01	3.01	<u>8.80</u>	2.52	<u>9.83</u>	9.00	2.81	8.31	1.96	<u>10.09</u>
Cu	7.82	1.02	<u>8.05</u>	3.94	5.90	8.54	1.58	7.51	2.17	5.85
Pb	0.45	0.27	<u>4.44</u>	18.60	<u>0.48</u>	0.65	0.24	<u>3.44</u>	13.77	0.59
Hg	0.04	0.01	0.03	0.02	0.03	0.08	0.15	0.04	0.02	0.04
Zn	83.0	14.5	<u>85.5</u>	18.1	<u>89.6</u>	91.8	17.9	86.3	16.3	87.1

Underlined concentrations are higher than pre-production averages

TABLE 4-7 Average and Standard Deviation Values for Pre-Production, Production, and Current Year *Nephtys* Data

Metal (mg/kg dw)	S-1 <i>Nephtys</i>					S-2 <i>Nephtys</i>				
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg	avg	stdev	avg	stdev	avg
Cd	3.91	1.72	2.90	0.89	3.27	1.40	0.85	1.15	0.50	0.97
Cu	9.27	1.41	<u>11.00</u>	6.65	5.45	11.21	3.56	9.05	4.04	5.30
Pb	0.45	0.16	<u>1.16</u>	1.01	0.44	0.50	0.26	<u>0.78</u>	0.44	<u>0.51</u>
Hg	0.05	0.01	0.04	0.02	0.05	0.02	0.01	<u>0.05</u>	0.25	<0.02
Zn	243.3	43.0	208.5	40.4	217.0	168.6	34.5	168.2	39.9	<u>189.0</u>

Metal (mg/kg dw)	S-4 <i>Nephtys</i>				
	pre-production (9/1984-8/1989)		production (9/1989 - 9/2011)		Current Year 2012
	avg	stdev	avg	stdev	avg
Cd	0.93	0.72	<u>1.08</u>	0.71	<u>0.96</u>
Cu	21.02	9.25	<u>24.13</u>	20.08	20.85
Pb	3.65	1.08	<u>11.43</u>	13.30	<u>4.05</u>
Hg	0.060	0.062	0.025	0.021	0.04
Zn	210.2	17.9	202.2	57.8	199.0

Underlined concentrations are higher than pre-production averages

Additional tissue samples of *Cockles* and *Littlenecks* were collected in 2012. Table 4-8 summarizes the average metal values for the available data for these additional tissue samples. Only *Cockles* at site S-4 has pre-production period data available for comparison (Table 4-8).

TABLE 4-8 Summary of Results for Additional Tissue Samples

Metal-average (mg/kg dw)	S-2 <i>Cockles</i>	S-2 <i>Littlenecks</i>	S-4 <i>Cockles</i>	
	(1999-2012)	(1999-2012)	(5/84-7/89)	(9/89-2012)
Cd	0.80	2.30	0.71	0.70
Cu	4.54	9.19	9.27	6.71
Pb	0.55	0.42	9.92	6.98
Hg	0.020	0.017	0.036	0.034
Zn	68.4	80.8	101.1	77.2

Effluent toxicity testing, conducted since the mining operations began, was discontinued in 2005 with re-issuance of the NPDES Permit (AK-004320-6). Over the 21 years of initially acute toxicity testing (February 1989 – October 1998), and then chronic toxicity testing (November 1998 – June 2005) no sublethal deleterious effects to tested marine aquatic organisms from prolonged exposure to the treated KGCMC effluent was determined to be likely:

“The data show that the effluent from Outfall 002 has no reasonable potential to contribute to an exceedence of the (Alaska) WQS for toxicity.” (USEPA Fact Sheet dated October 28, 2004; page 14, Section VI.B Whole Effluent Toxicity Testing).

4.3 QA/QC Results

Columbia Analytical Services (CAS) analyzed the required parameters (see Table 1-1) in the bioassay samples. Complete QA plans and reports are kept on file in the lab's office and are available upon request. The remainder of this section summarizes the relevant QA/QC results for the spring and fall sampling events in 2012.

Spring 2012:

The Relative Percent Difference (RPD) for the replicate analysis of mercury in the Batch QCI sample was outside the normal CAS control limits. The variability in the results was attributed to the heterogeneous distribution of mercury in the sample. The samples were homogenized, freeze dried, and then ground prior to digestion; however this was not sufficient to achieve a completely uniform distribution of these analytes in the tissue.

Fall 2012:

The control criteria for matrix spike recovery of zinc for sample S-1 Nephthys I were not applicable. The analyte concentration in the sample was significantly higher than the added spike concentration, preventing accurate evaluation of the spike recovery.

Beginning in the fall of 2004, duplicate samples have been collected from each site, where possible, to address a National Marine Fisheries Service request. Precision can be calculated from the results of duplicate samples. In this case, the relative standard deviation RSD (the standard deviation relative to the mean, expressed as a percent) is shown for the duplicate samples in Table 4-9. The data quality objectives for the RSD are less than or equal to 30 percent, when the values are at least four times the detection limit. One out of the 24 (approximately 4 percent) of the RSDs calculated for the 2012 duplicate samples was not within this data quality objective.

TABLE 4-9 Relative Standard Deviation (RSD) for Duplicate Tissue Samples*-- Indicates the RSD was not calculated because one or more of the results was not greater than four times the detection limit (DL)*

SAMPLE ID	DATE	Cd (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	Hg (mg/kg dw)	Zn (mg/kg dw)
		0.02	0.1	0.02	0.02	0.5
S-1 Nepthys I	5/5/12	2.47	5.4	0.44	0.03	178
S-1 Nepthys II	5/5/12	2.33	6.8	0.47	0.03	211
S-1 Nepthys III	5/5/12	2.37	7.4	0.52	0.04	198
RSD		3.02	15.7	8.5	--	8.5
S-2 Nepthys I	5/5/12	0.91	5.6	0.56	<0.02	185
S-2 Nepthys II	5/5/12	0.99	6.1	0.48	0.02	181
S-2 Nepthys III	5/5/12	0.91	6.7	0.51	0.02	188
RSD		4.9	9.0	7.8	--	1.9
S-4 Nepthys I	5/7/12	0.39	6.0	3.76	<0.03	175
S-4 Nepthys II	5/7/12	0.32	3.9	3.71	<0.02	175
S-4 Nepthys III	5/7/12	0.42	4.9	3.93	0.02	183
RSD		13.6	21.3	3.03	--	2.6
S-1 Nepthys I	8/29/12	4.07	5.5	0.44	0.07	256
S-1 Nepthys II	8/29/12	3.64	5.3	0.39	0.09	523
S-1 Nepthys III	8/29/12	3.34	5.9	0.37	0.06	206
RSD		9.96	5.5	9.0	--	11.8
S-2 Nepthys I	8/29/12	1.02	5.0	0.48	<0.02	193
S-2 Nepthys II	8/29/12	0.94	6.7	0.50	<0.02	198
S-2 Nepthys III	8/29/12	0.87	5.6	0.48	<0.02	192
RSD		8.0	15	2.4	--	1.7
S-4 Nepthys I	8/28/12	1.53	35.7	4.34	0.07	223
S-4 Nepthys II	8/28/12	1.25	19.8	5.20	0.03	215
S-4 Nepthys III	8/28/12	1.03	16.7	5.03	0.03	206
RSD		19.7	42.4	9.4	--	10

5.0 CONCLUSIONS

The current status of the health of marine and aquatic ecosystems can be viewed based on the number of types of species present in an area (species diversity, or “biodiversity”), the number of individuals from each species in an area (species abundance), and quality of the environment (habitat integrity relative to pristine conditions).

For the marine environment, there are no data available to numerically compare diversity or abundance of organisms between pre-mining and post-mining years. Observations by fishermen and researchers suggest that the physical features and biotic communities of Hawk Inlet remain intact following over a decade of operation of the mine and they remain similar to adjacent inlets (Ridgeway, 2003). Halibut and crab numbers are reported to have declined significantly with the closing of the fish processing facilities which previously operated at the now Hawk Inlet Cannery which currently provides the HGCMC port facilities.

Marine species which consume sedentary seafloor organisms such as worms and bivalves would be most susceptible to trophic transfer of some metals. Based on the suite of species listed as having Essential Fish Habitat in Hawk Inlet, the species most likely to encounter these elevated metal levels through their diet and habitat uses would include the flatfishes (*e.g.* yellowfin sole, arrowtooth flounder, flathead sole, and rock sole), pacific cod, sculpin and crab species. Pacific halibut also have similar consumption patterns to these species. All of these species consume worms, bivalves, and crab.

Other migratory and resident fish, mammals, and birds which consume seafloor-dwelling organisms near the ore loading dock would also likely encounter elevated metal levels in their diet in restricted sites within Hawk Inlet. There are no data available to evaluate whether metals are increasing through trophic transfer, or biomagnification at higher trophic levels in Hawk Inlet marine species such as fish, crab and mammals. However, given the mobility of the afore-mentioned species, and the restricted HGCMC-associated locations of higher metal loading, it is unlikely that any of these species would show a significant effect attributable to mining activities in the vicinity of Hawk Inlet.

6.0 REFERENCES

Greens Creek Tailings Disposal: Final Environmental Impact Statement; USDA Forest Service, November 2003.

Kennecott Greens Creek Mining Company, Hawk Inlet Monitoring Program 2005 Annual Report, January 2006.

Kennecott Greens Creek Mining Company, Hawk Inlet Monitoring Program 2006 Annual Report, April 2007.

Kennecott Greens Creek Mining Company, Hawk Inlet Monitoring Program 2007 Annual Report, January 2008.

Hecla Greens Creek Mining Company, Hawk Inlet Monitoring Program 2008 Annual Report, January 2009.

Hecla Greens Creek Mining Company, Hawk Inlet Monitoring Program 2009 Annual Report, January 2010.

Hecla Greens Creek Mining Company, Hawk Inlet Monitoring Program 2010 Annual Report, January 2011.

Hecla Greens Creek Mining Company, Hawk Inlet Monitoring Program 2011 Annual Report, January 2012.

Kennecott Greens Creek Mine Risk Assessment NPDES Permit No. AK-004320-6, Admiralty Island, Alaska, Oregon Institute of Oceanography, and Remediation Technologies, Inc. June 22, 1998.

Marine Taxonomic Services Ltd, Hawk Inlet Facilities Year 2012 Annual Inspection Report, May 2012.

National Pollutant Discharge Elimination System (NPDES) permit AK-004320-6, USEPA, effective date July 1, 2005.

NPDES Quality Assurance Project (QAP), KGCMC, December 2009.

Oregon Institute of Oceanography (OIO) 1984 – 2002. Laboratory Results of Semi-Annual NPDES sediment and mussel tissue sampling in Hawk Inlet, Alaska. Columbia Analytical Lab Data for years 1984-2002.

Technical Review of the Status of Essential Fish Habitat in Hawk Inlet Subsequent to Mining Operations, M. Ridgeway, Oceanus Alaska, October 2003.

FIGURES

FIGURE 1-1 Aerial Photo of Lower Hawk Inlet, Admiralty Island with Water, Sediment and Tissue Sampling Site Locations



NOTES: Sites 106, 107 and 108 are sea water sampling sites.
 S-1, S-2, S-4 and S-5 are sediment and *Nephtys* and *Nereis* sampling sites.
 (Station S-3 – not shown – is at the head of Hawk Inlet.)
 Stations 1, 2, 3 and ESL are mussel sampling sites.

Figure 2-1a

Site 106 - Field pH

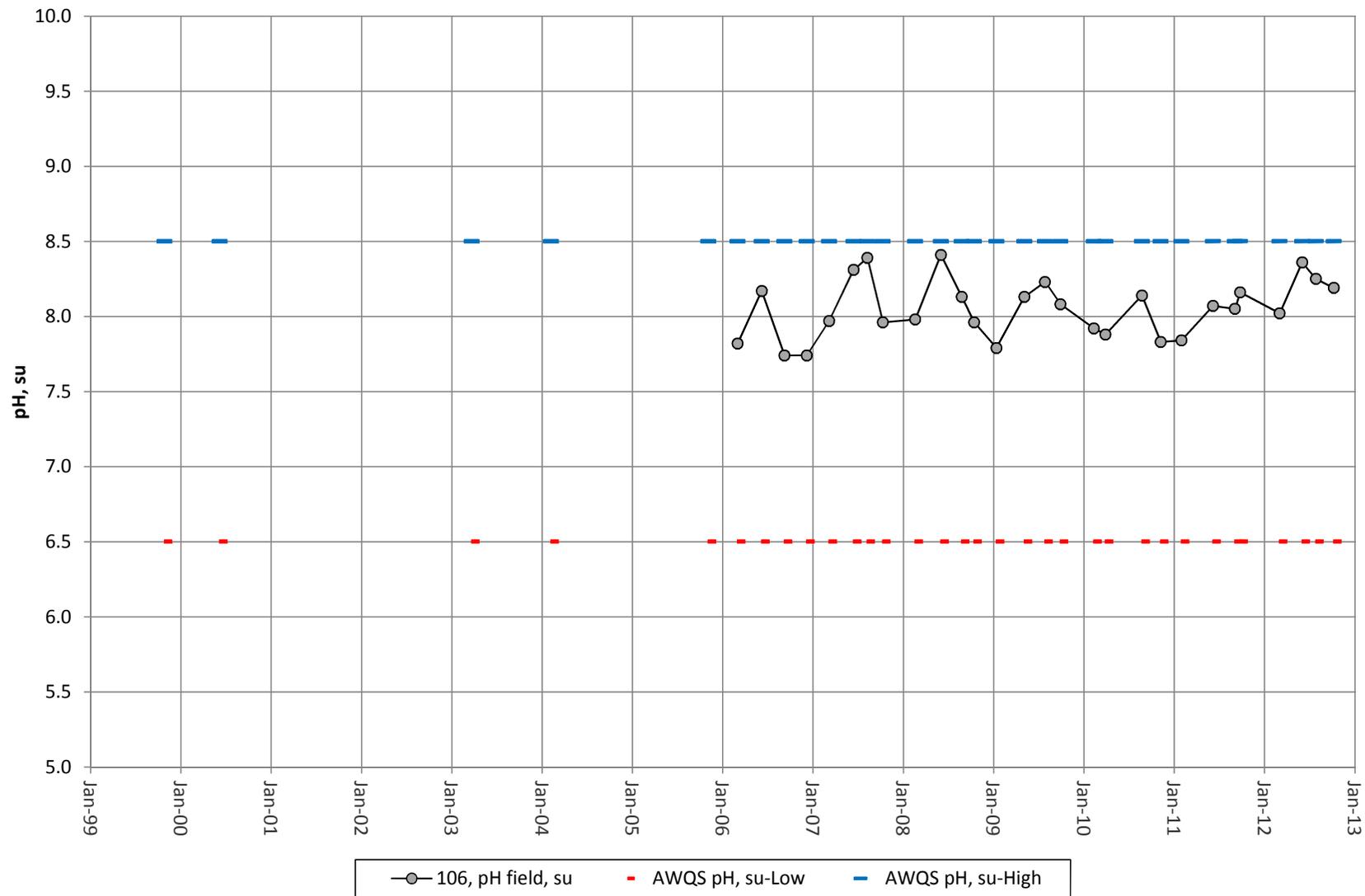


Figure 2-1b

Site 107 - Field pH

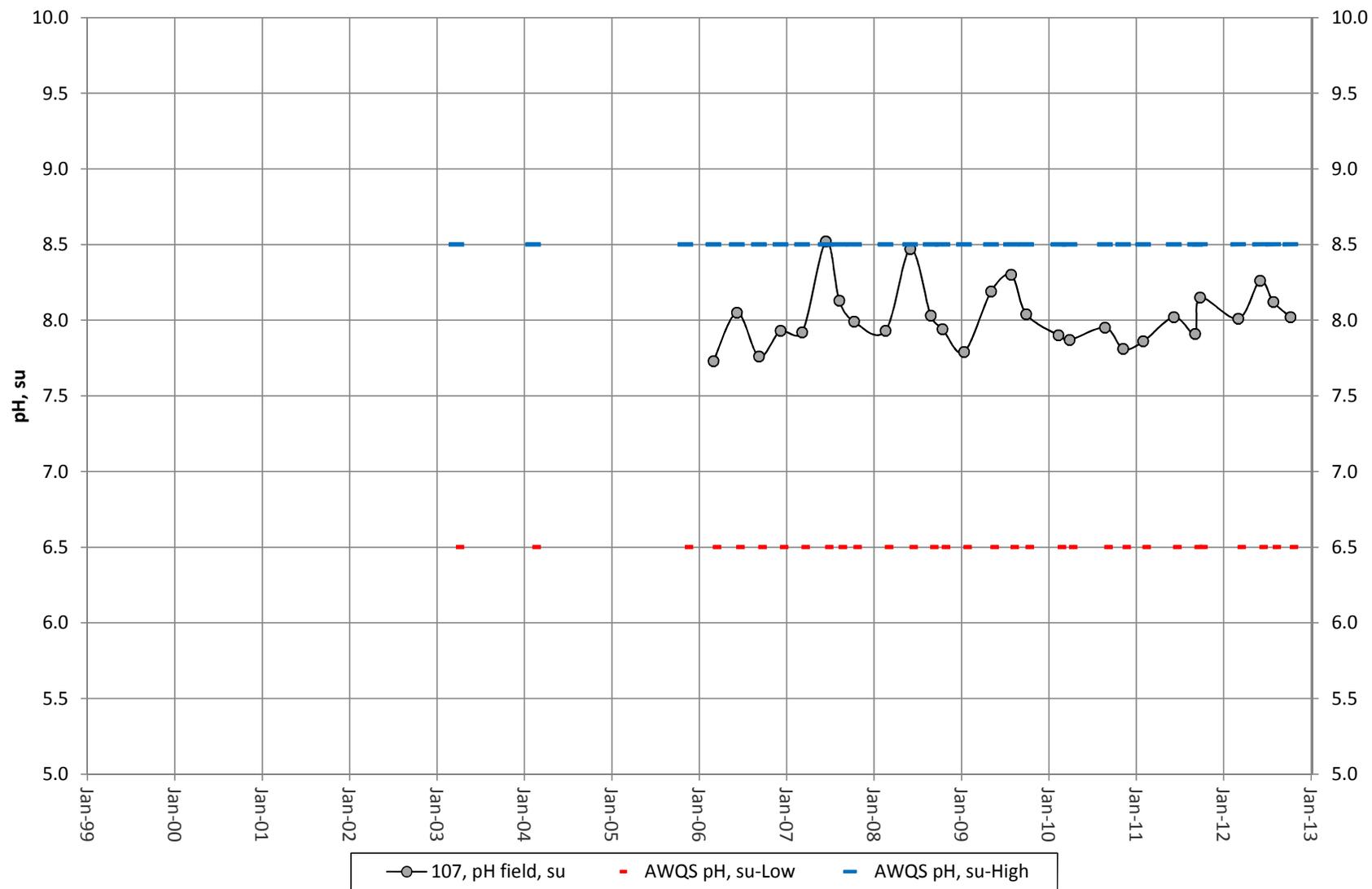


Figure 2-1c

Site 108 - Field pH

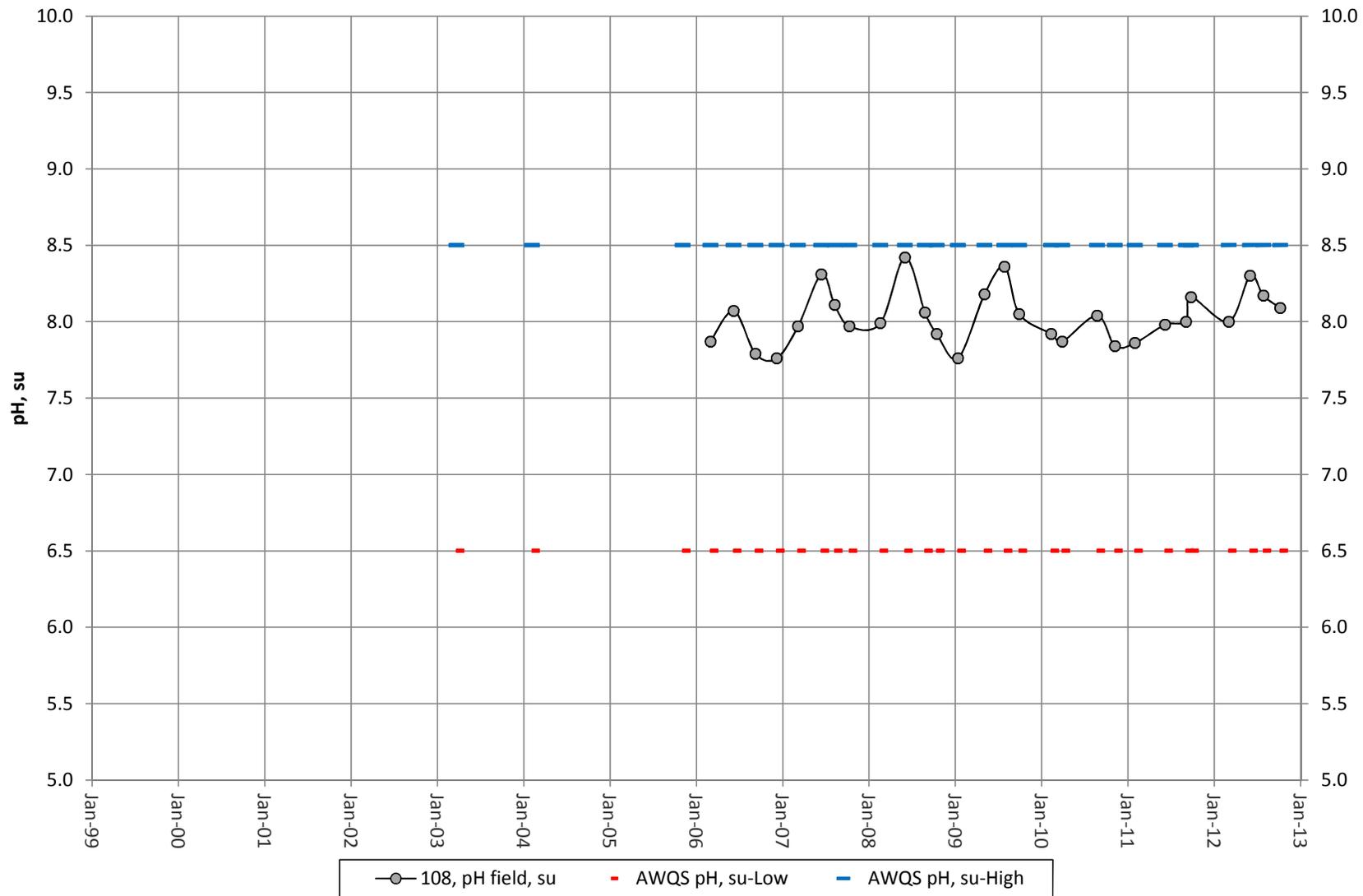


Figure 2-2a

Site 106 - Field Conductivity

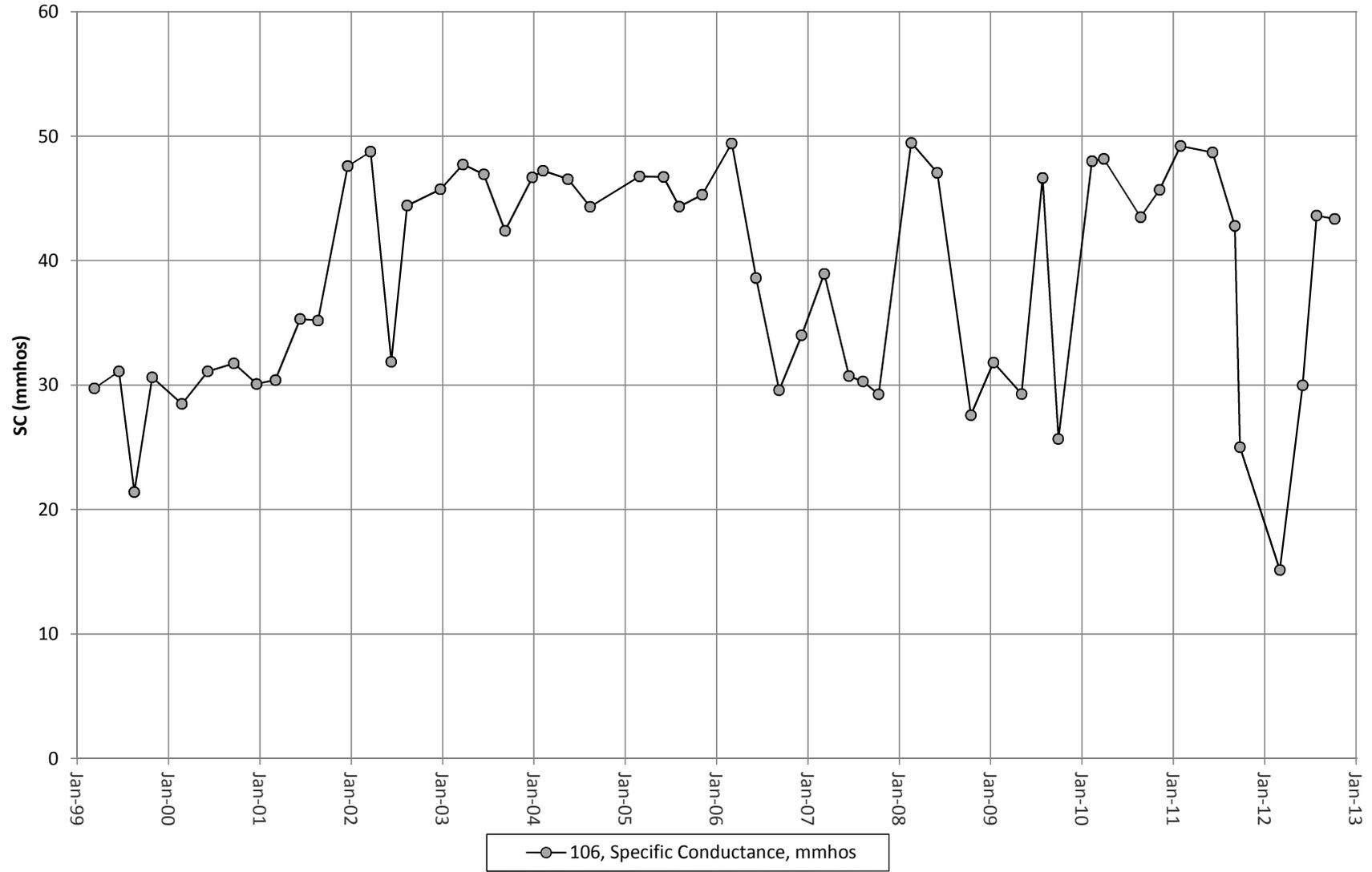


Figure 2-2b

Site 107 - Field Conductivity

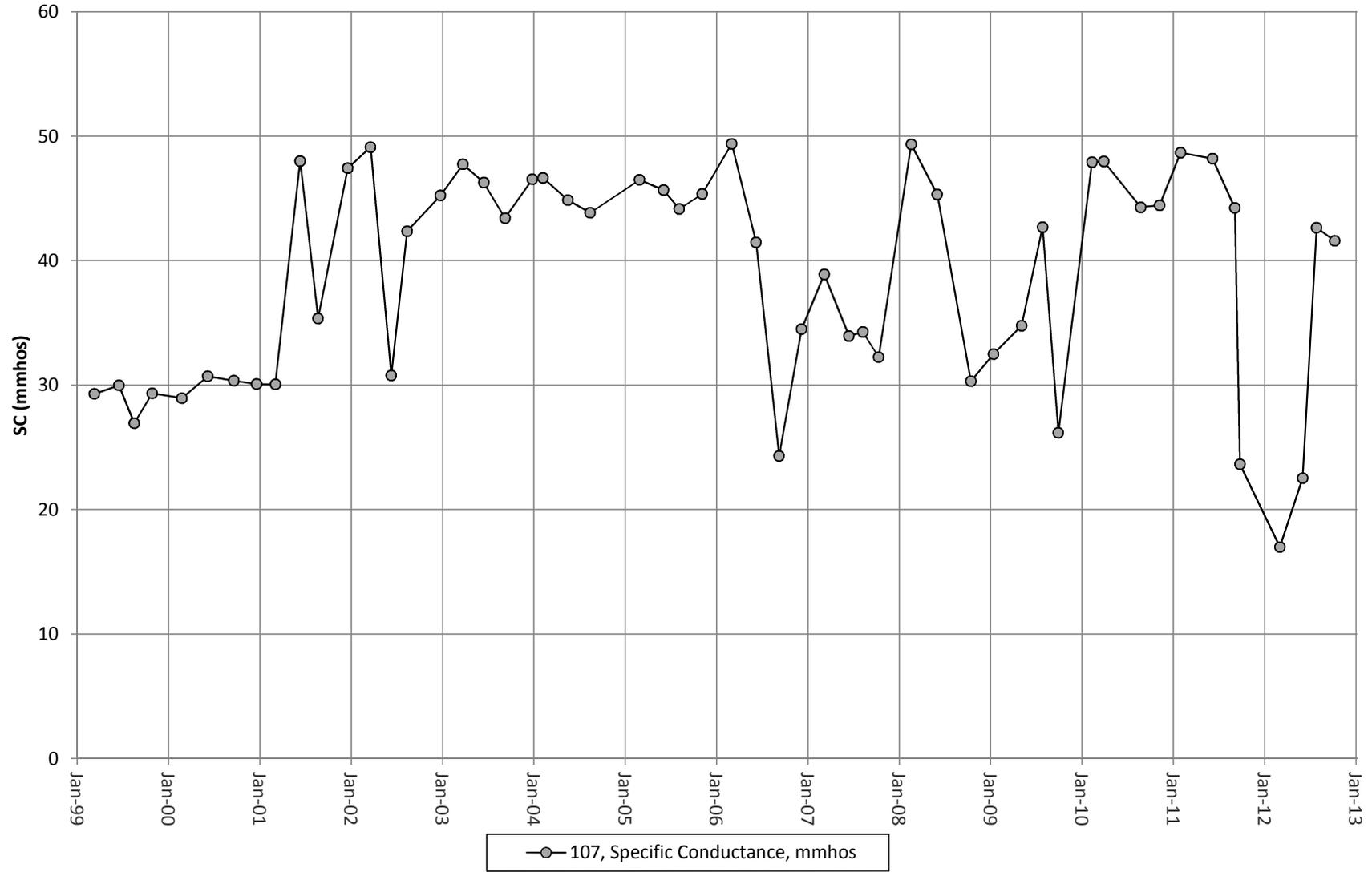


Figure 2-2c

Site 108 - Field Conductivity

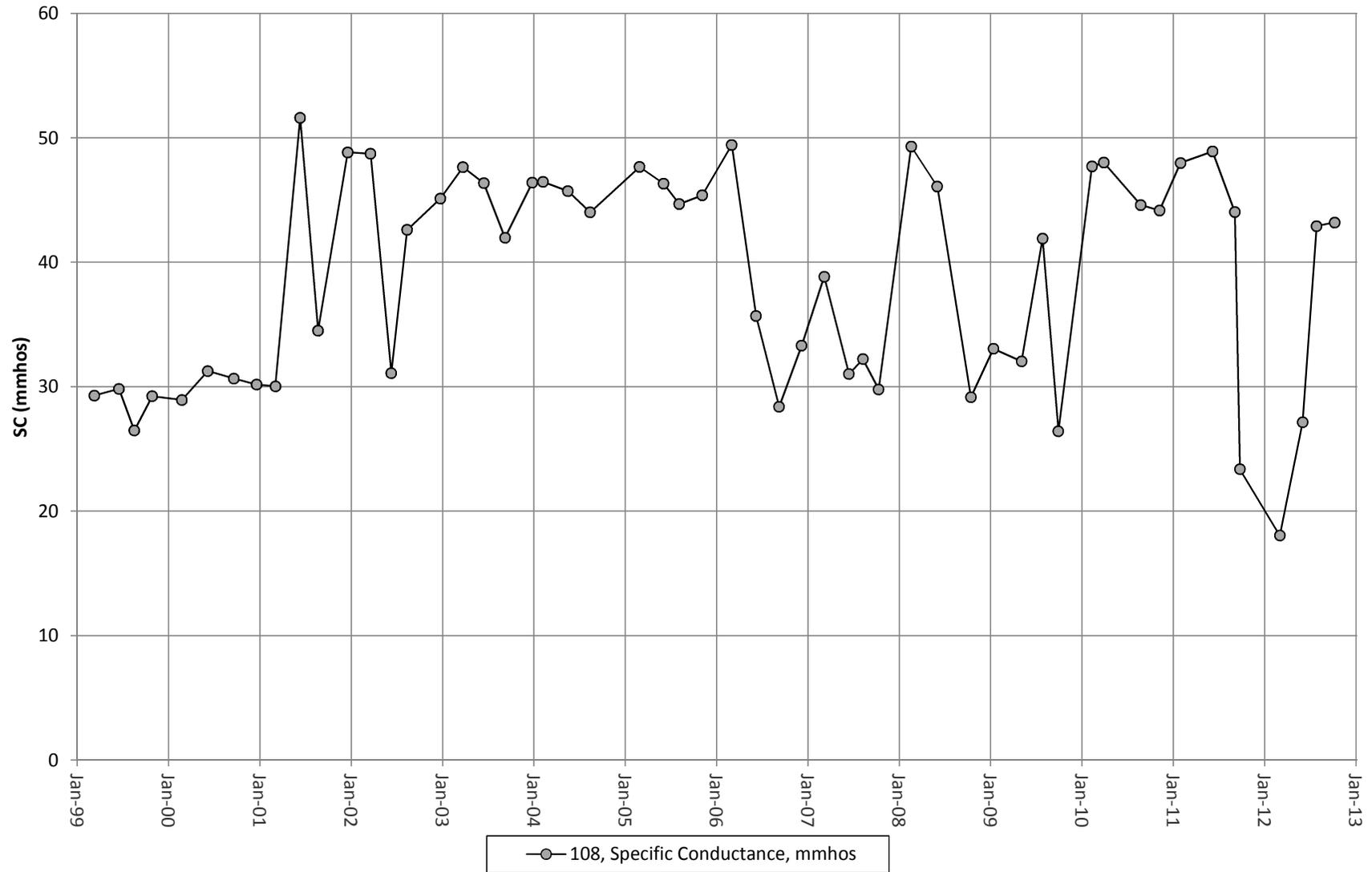


Figure 2-3a

Site 106 - Cadmium

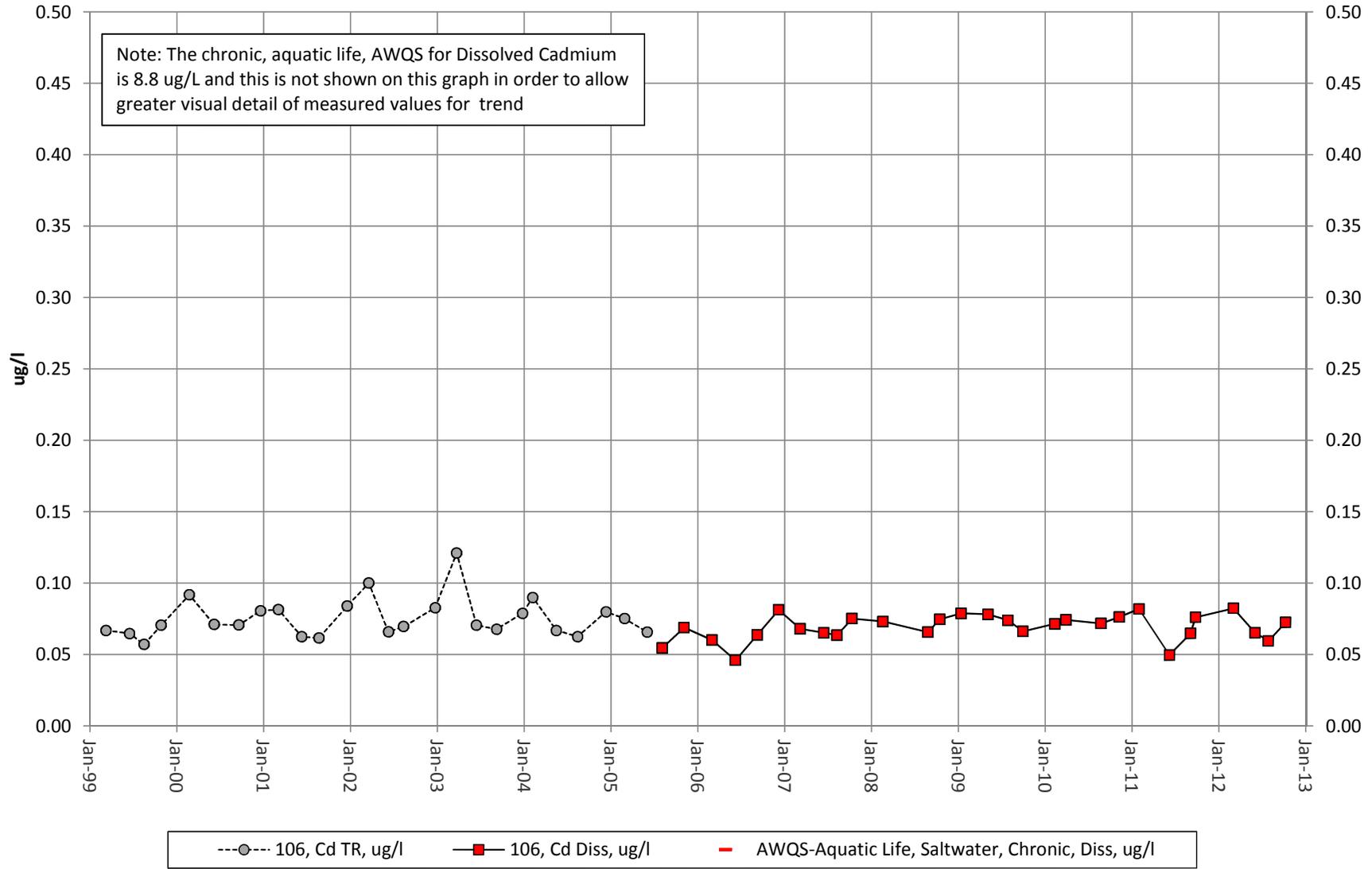


Figure 2-3b

Site 107 - Cadmium

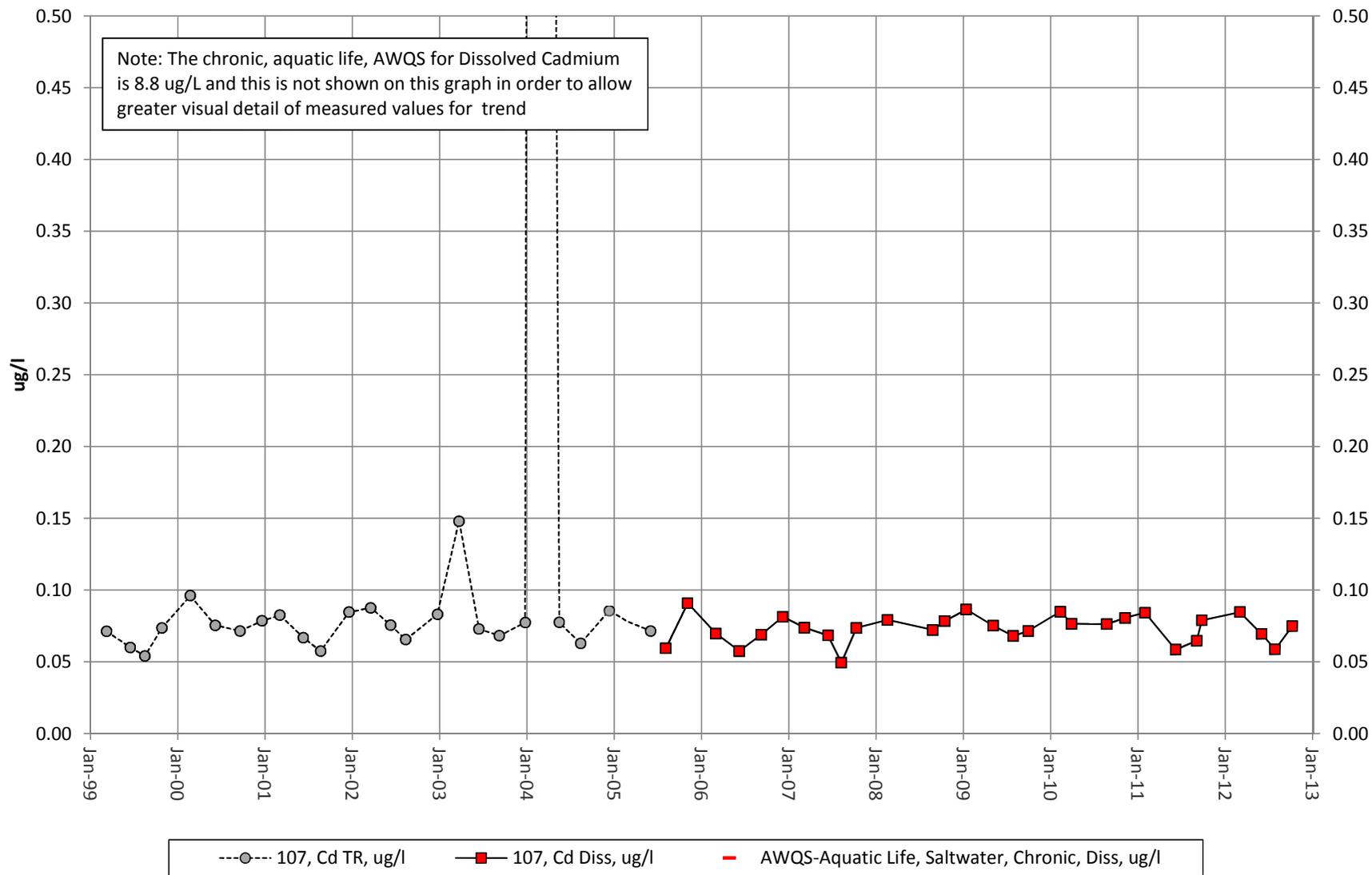


Figure 2-3c

Site 108 - Cadmium

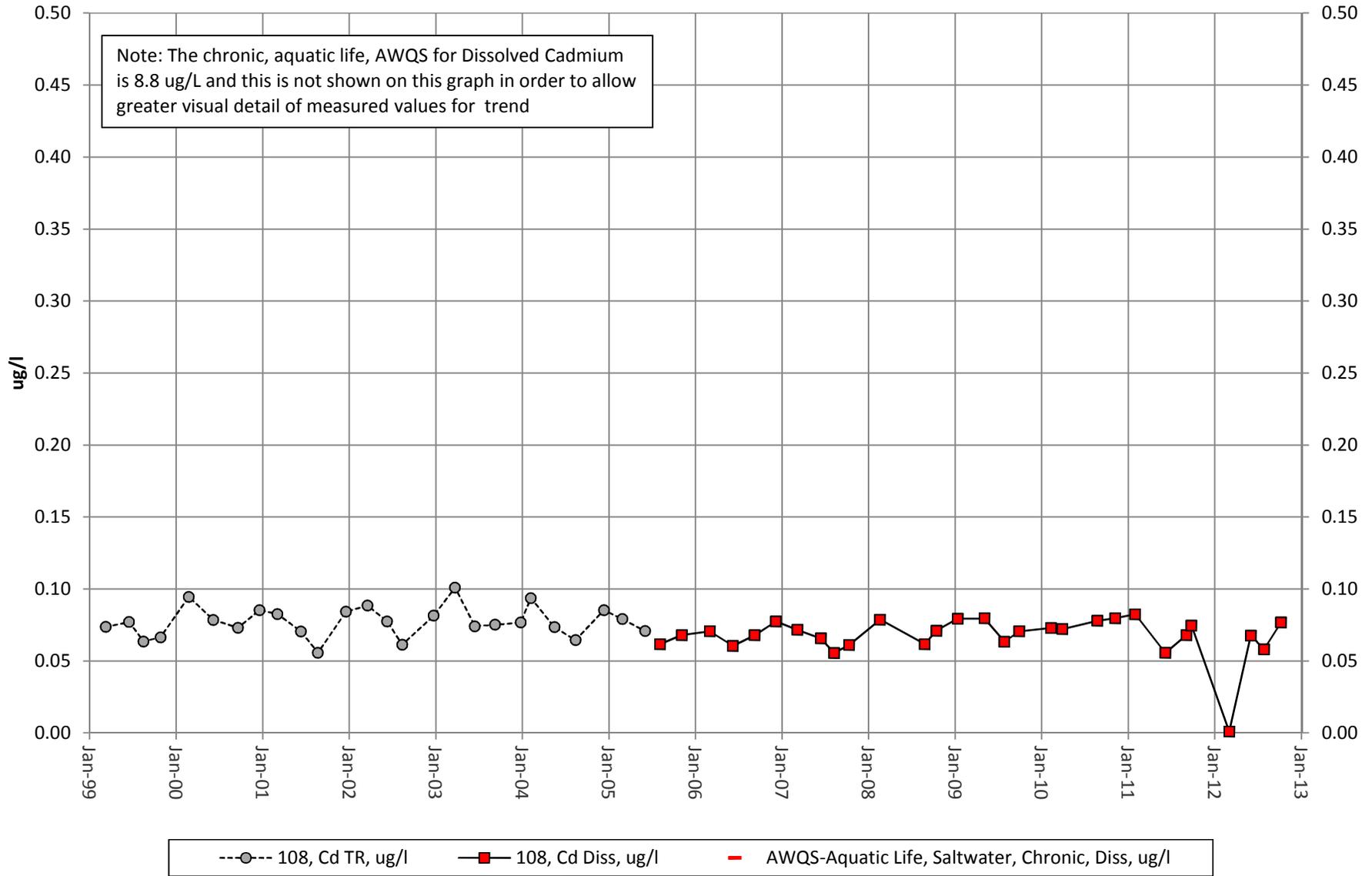


Figure 2-4a

Site 106 - Copper

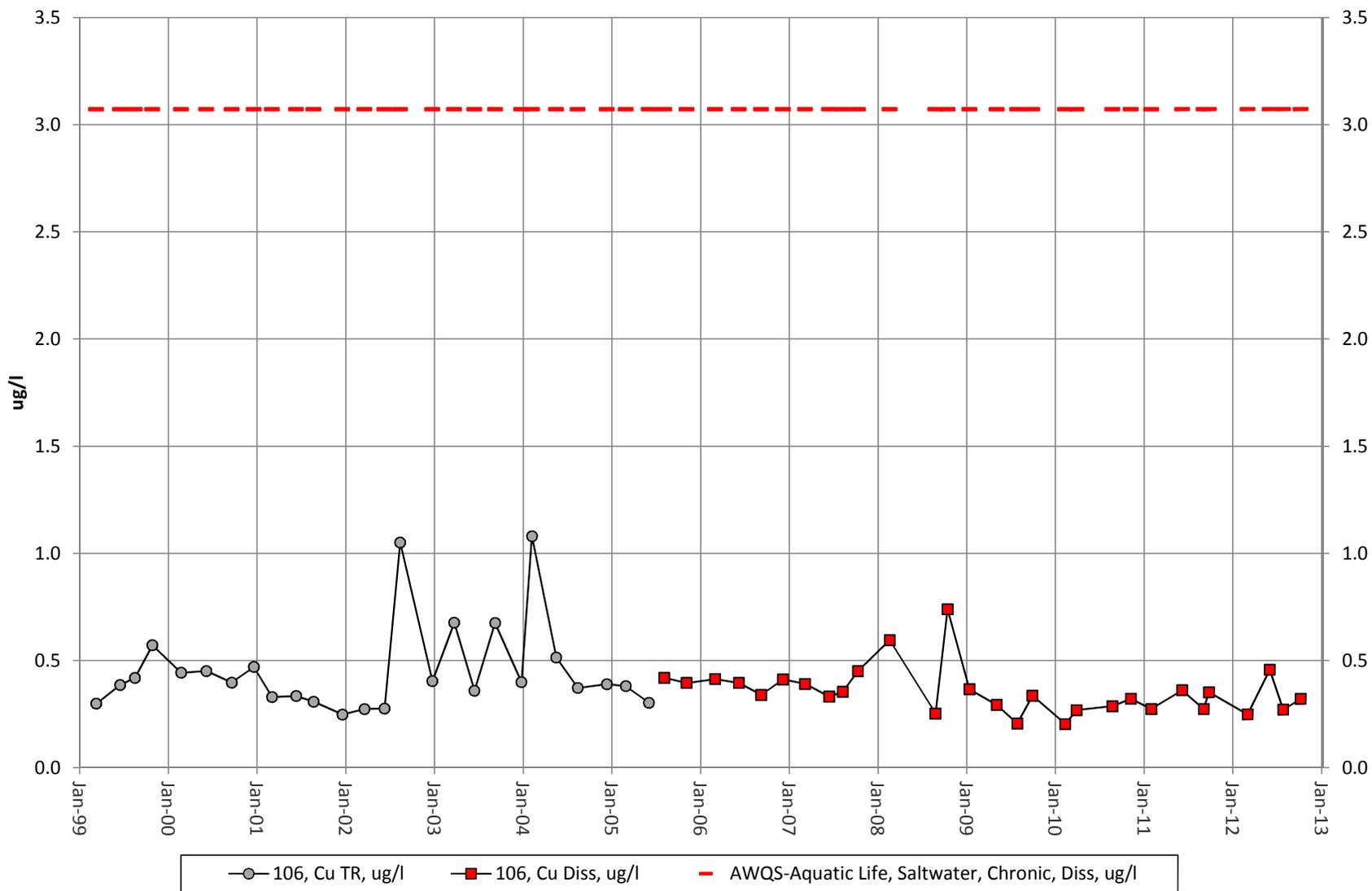


Figure 2-4b

Site 107 - Copper

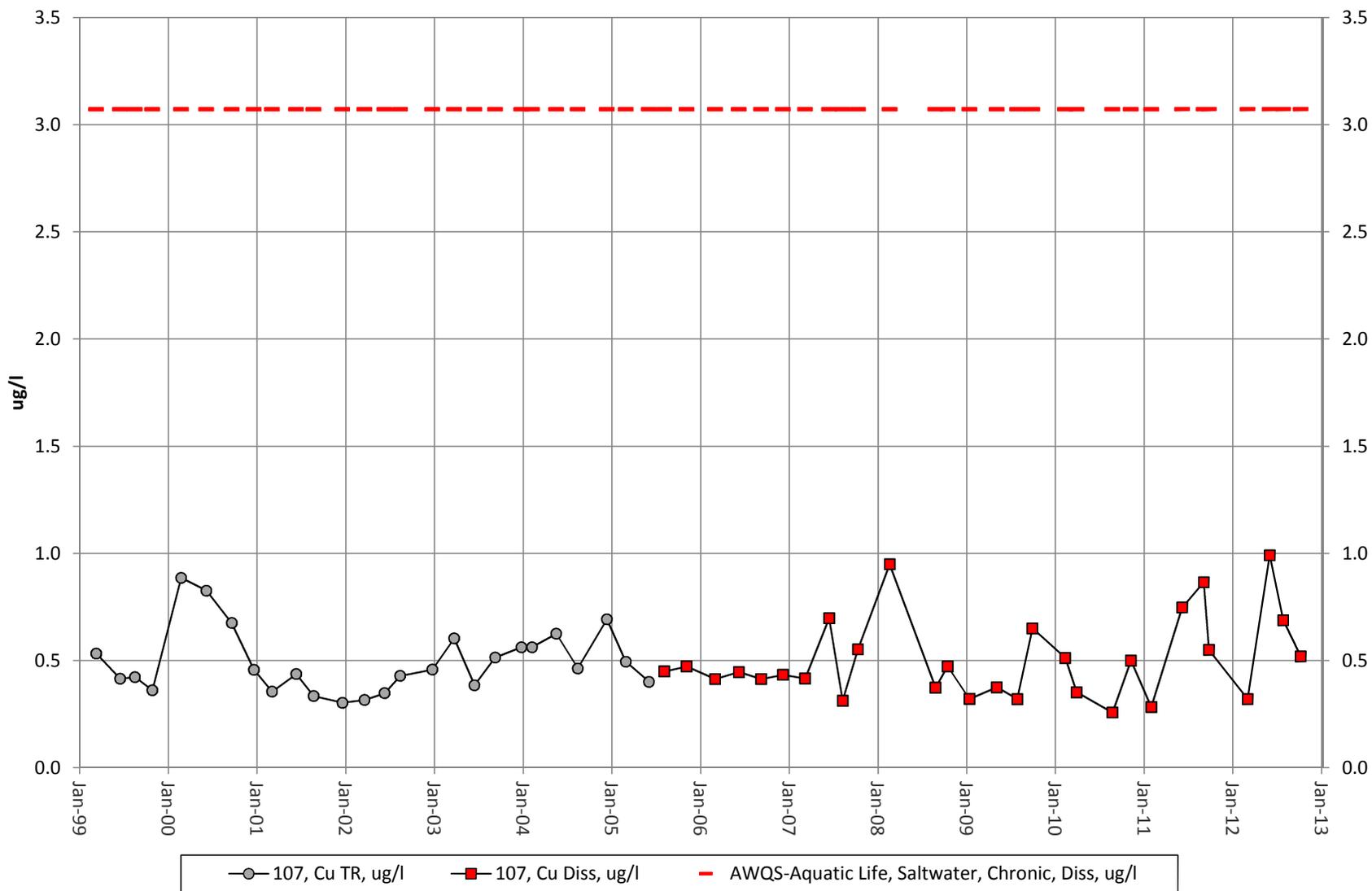


Figure 2-4c

Site 108 - Copper

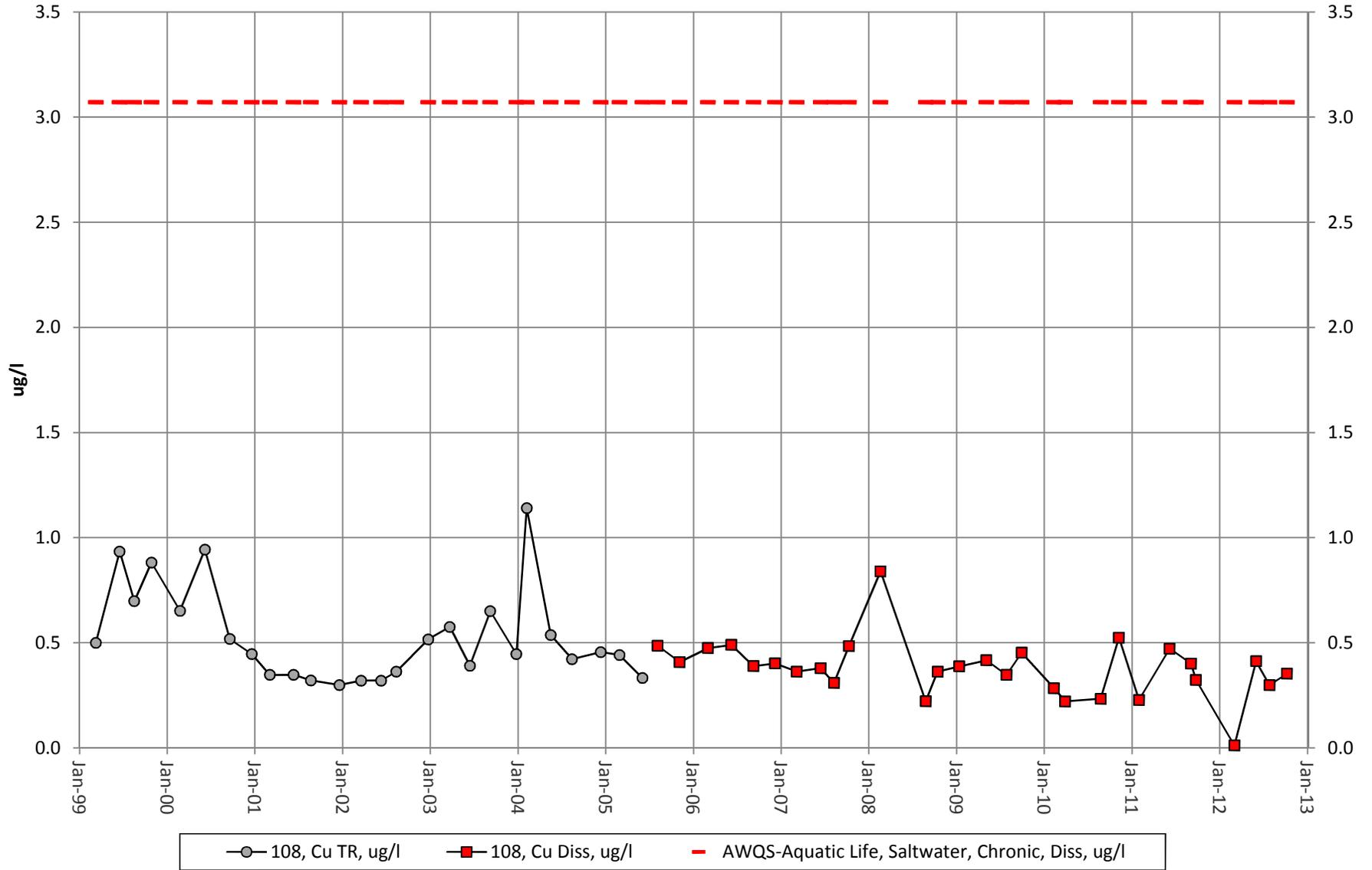


Figure 2-5a

Site 106 - Mercury

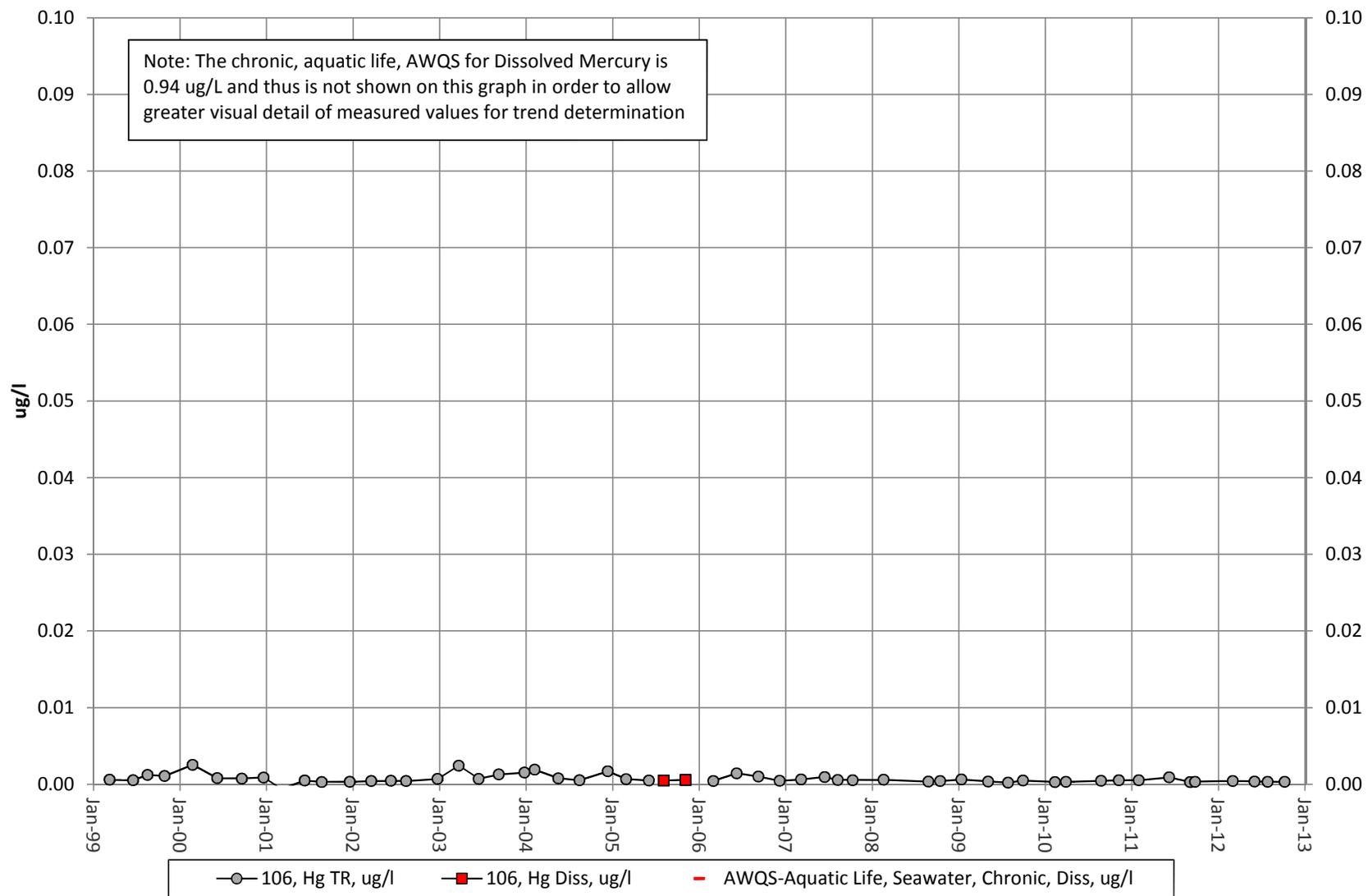


Figure 2-5b

Site 107 - Mercury

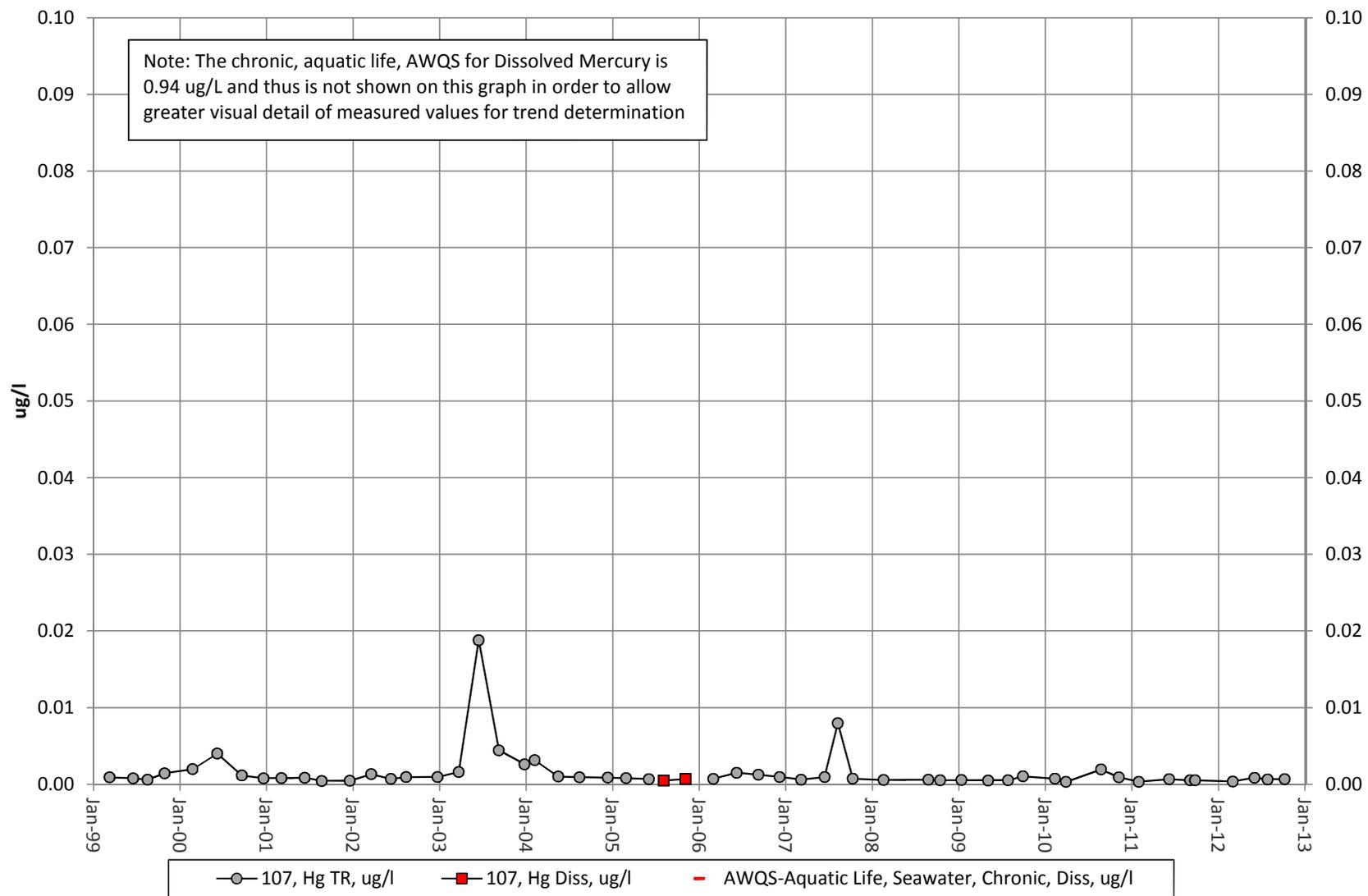


Figure 2-5c

Site 108 - Mercury

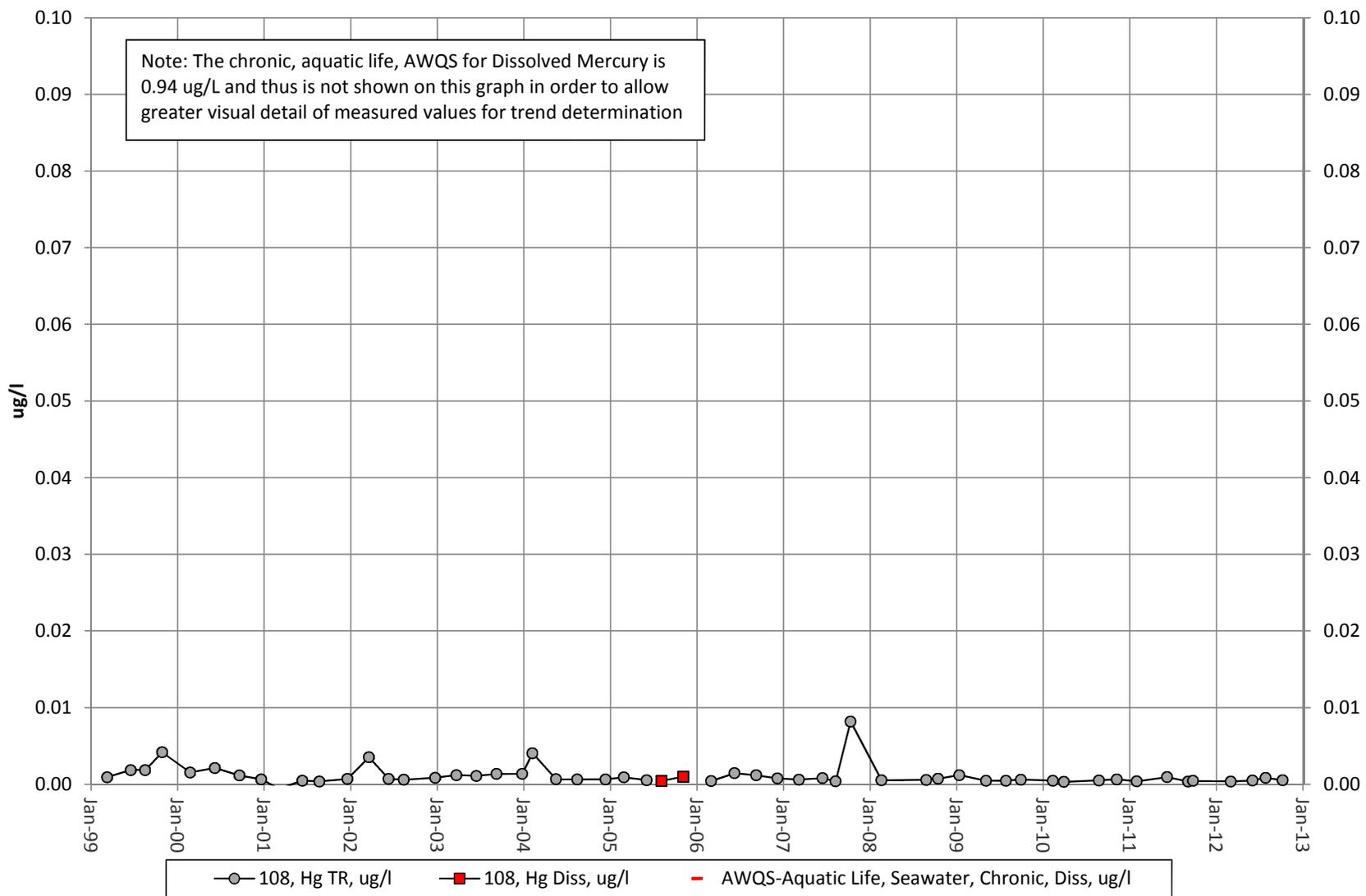


Figure 2-6a

Site 106 - Lead

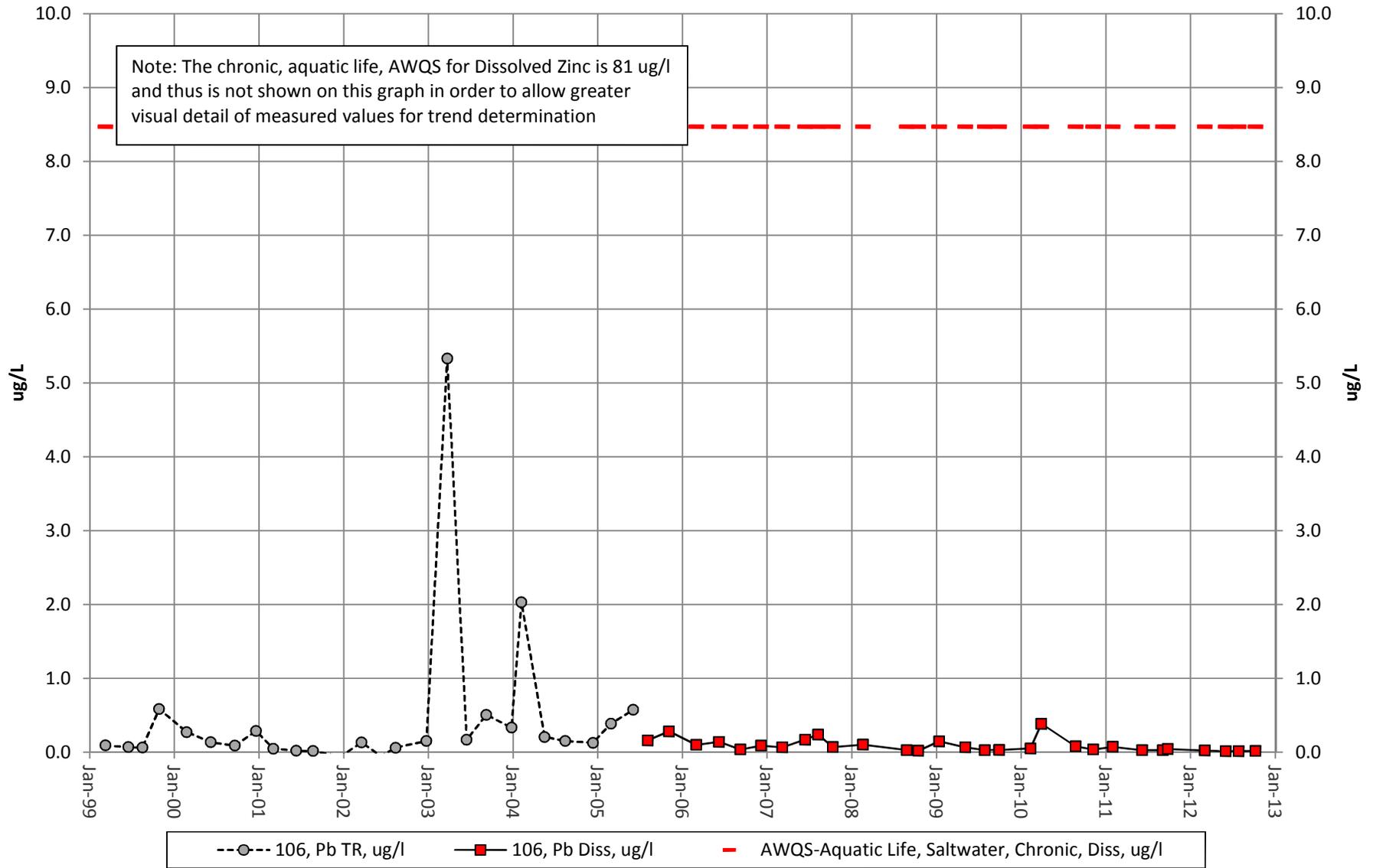


Figure 2-6b

Site 107 - Lead

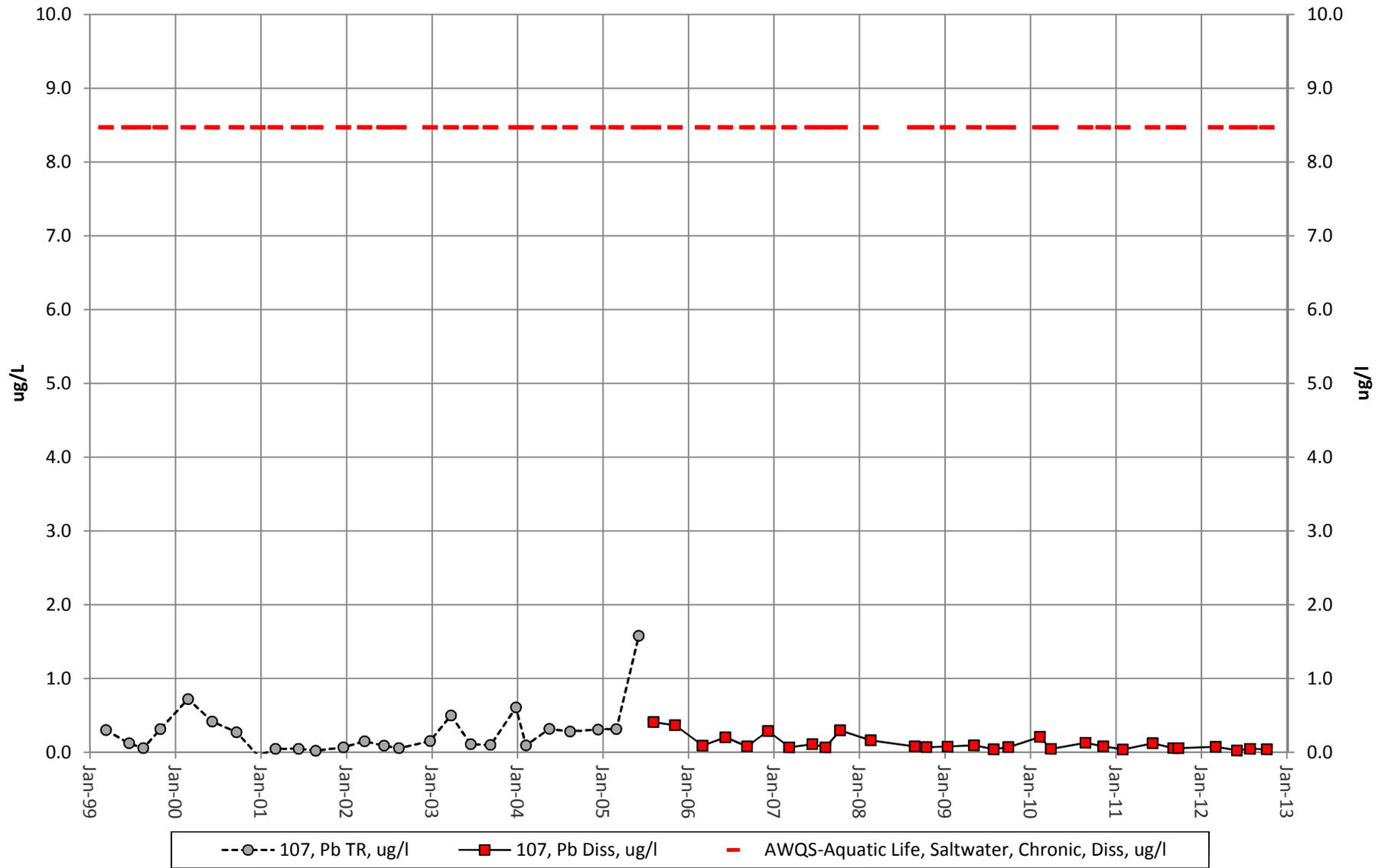


Figure 2-6c

Site 108 - Lead

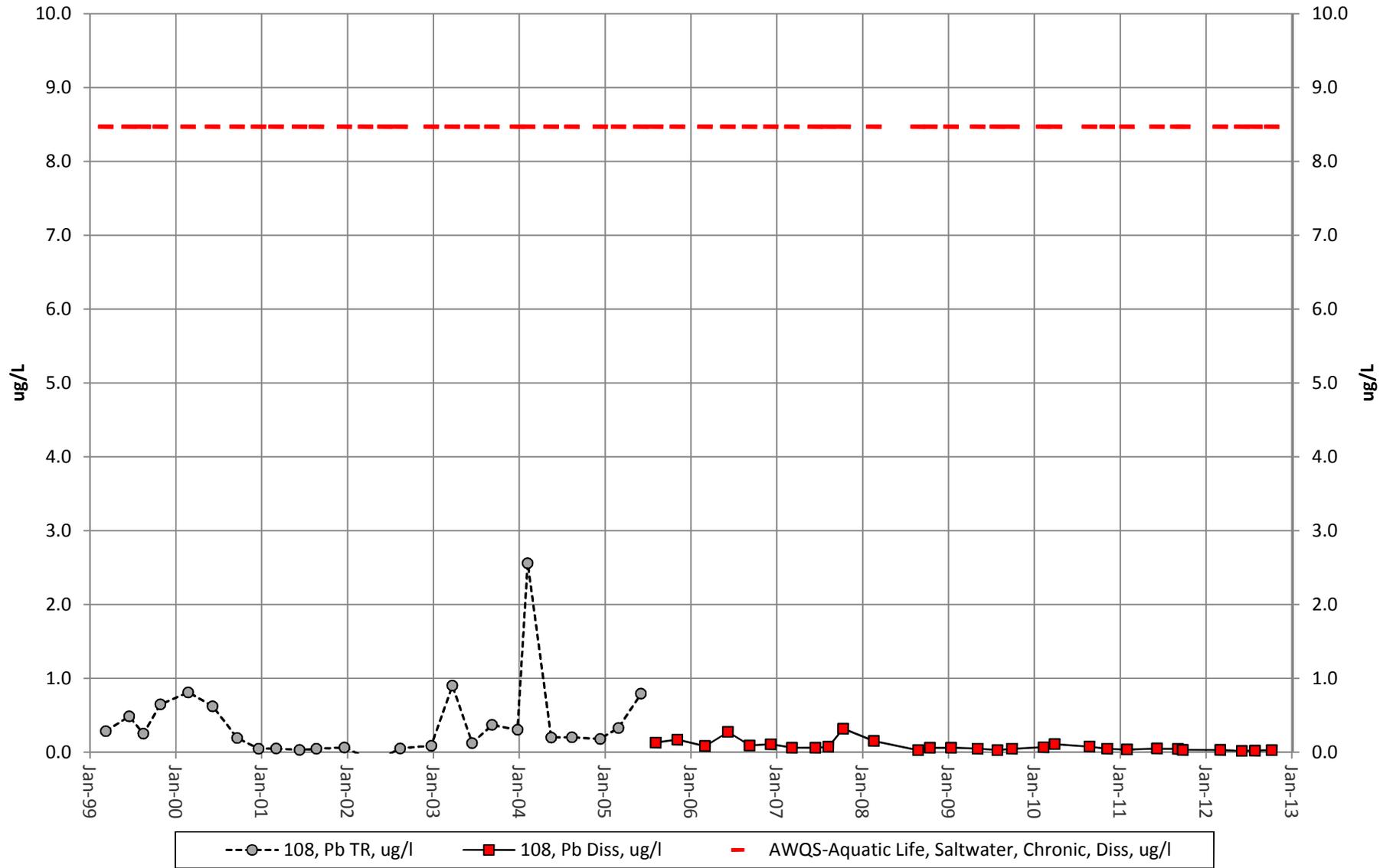


Figure 2-7a

Site 106 - Zinc

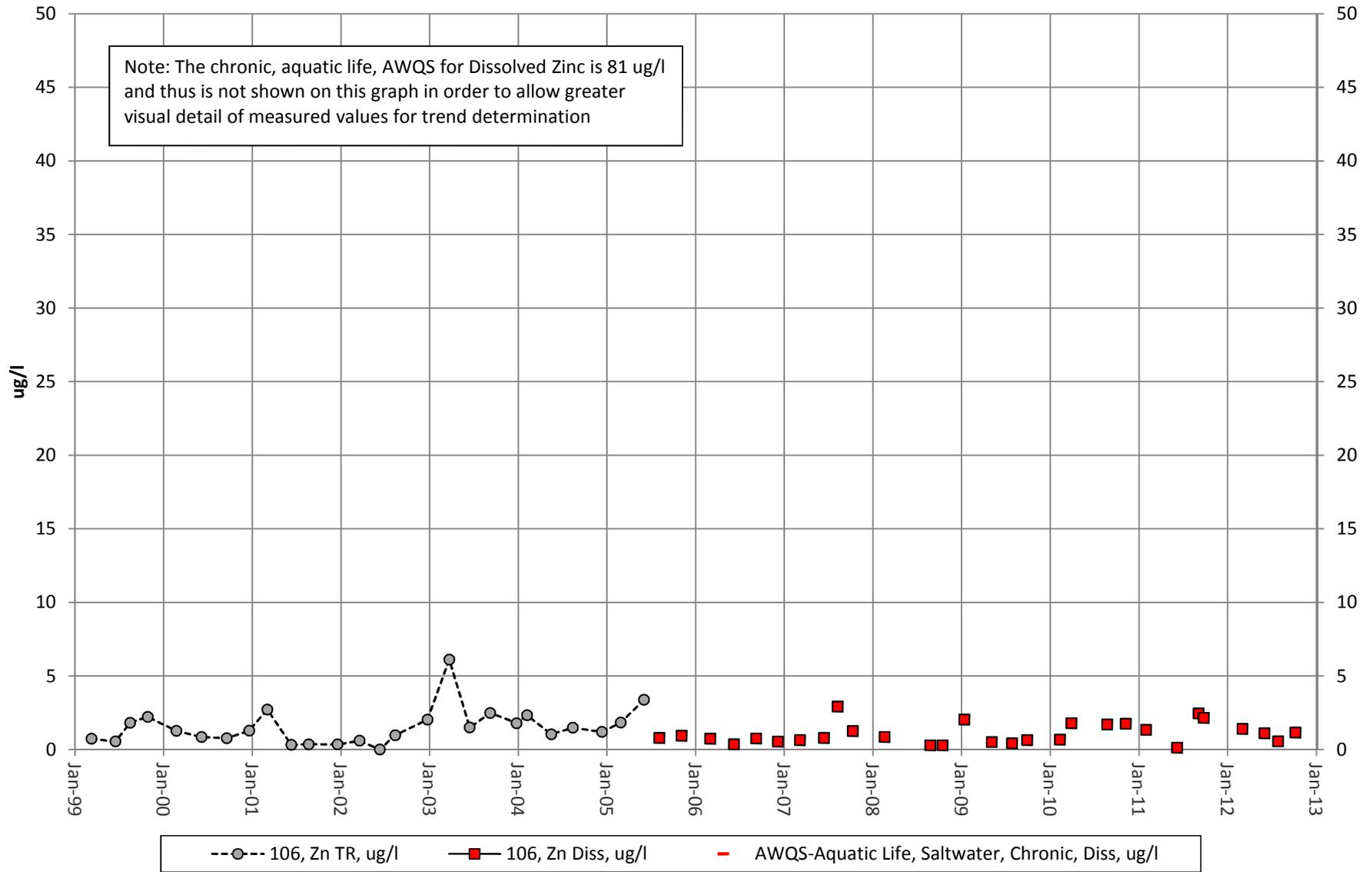


Figure 2-7b

Site 107 - Zinc

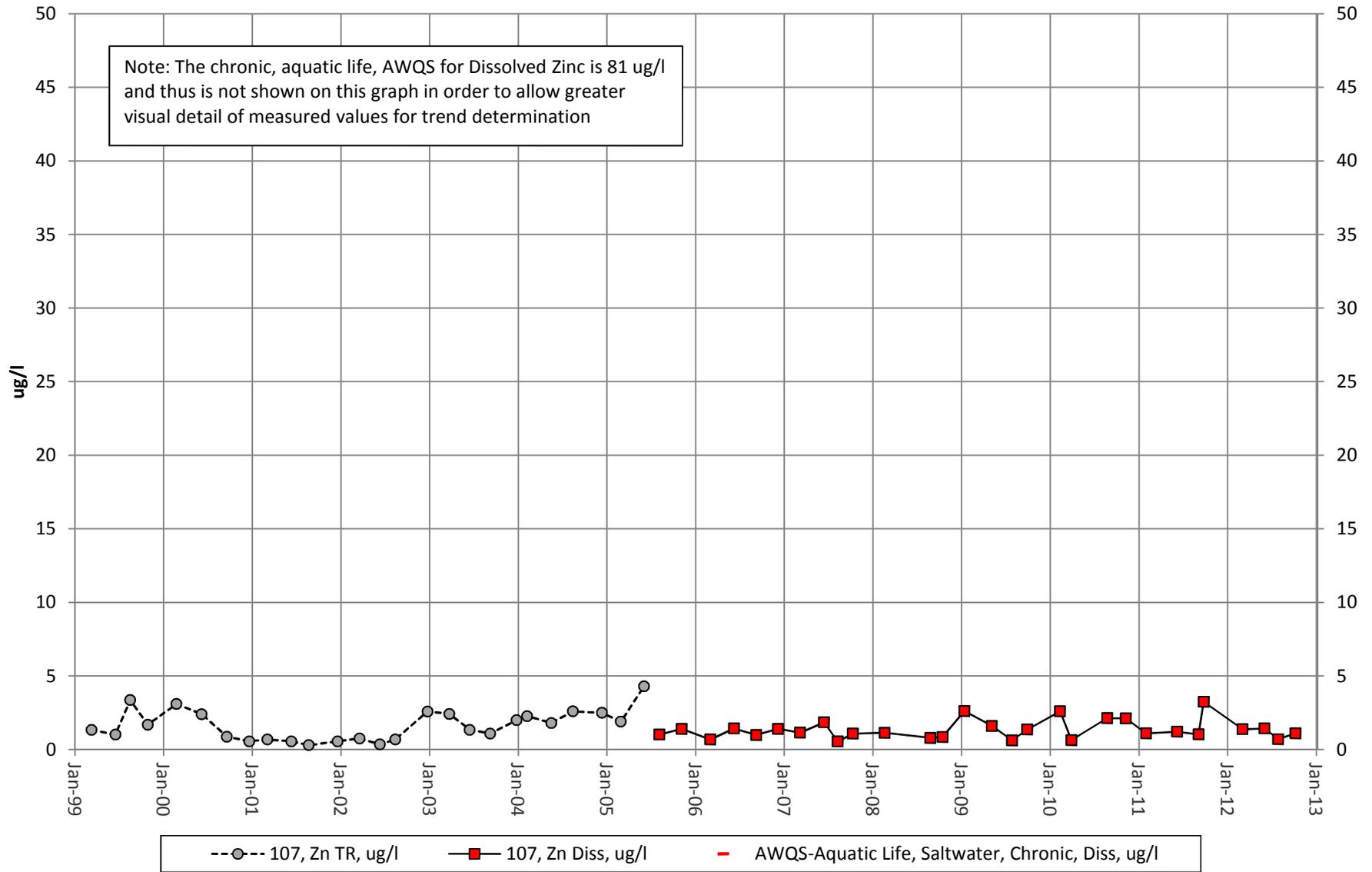


Figure 2-7c

Site 108 - Zinc

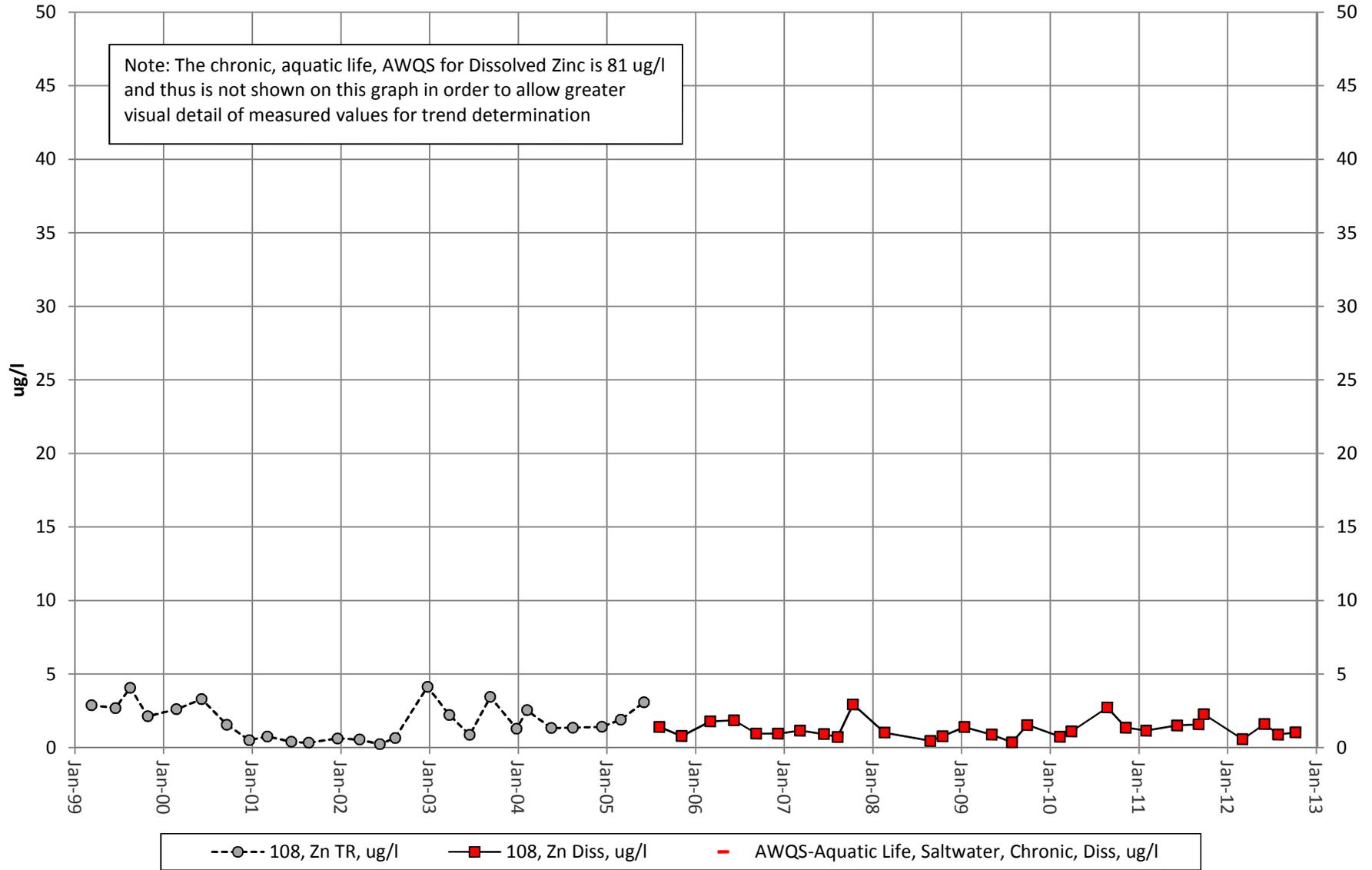


FIGURE 3-1

CADMIUM IN SEDIMENTS S-1 and S-2

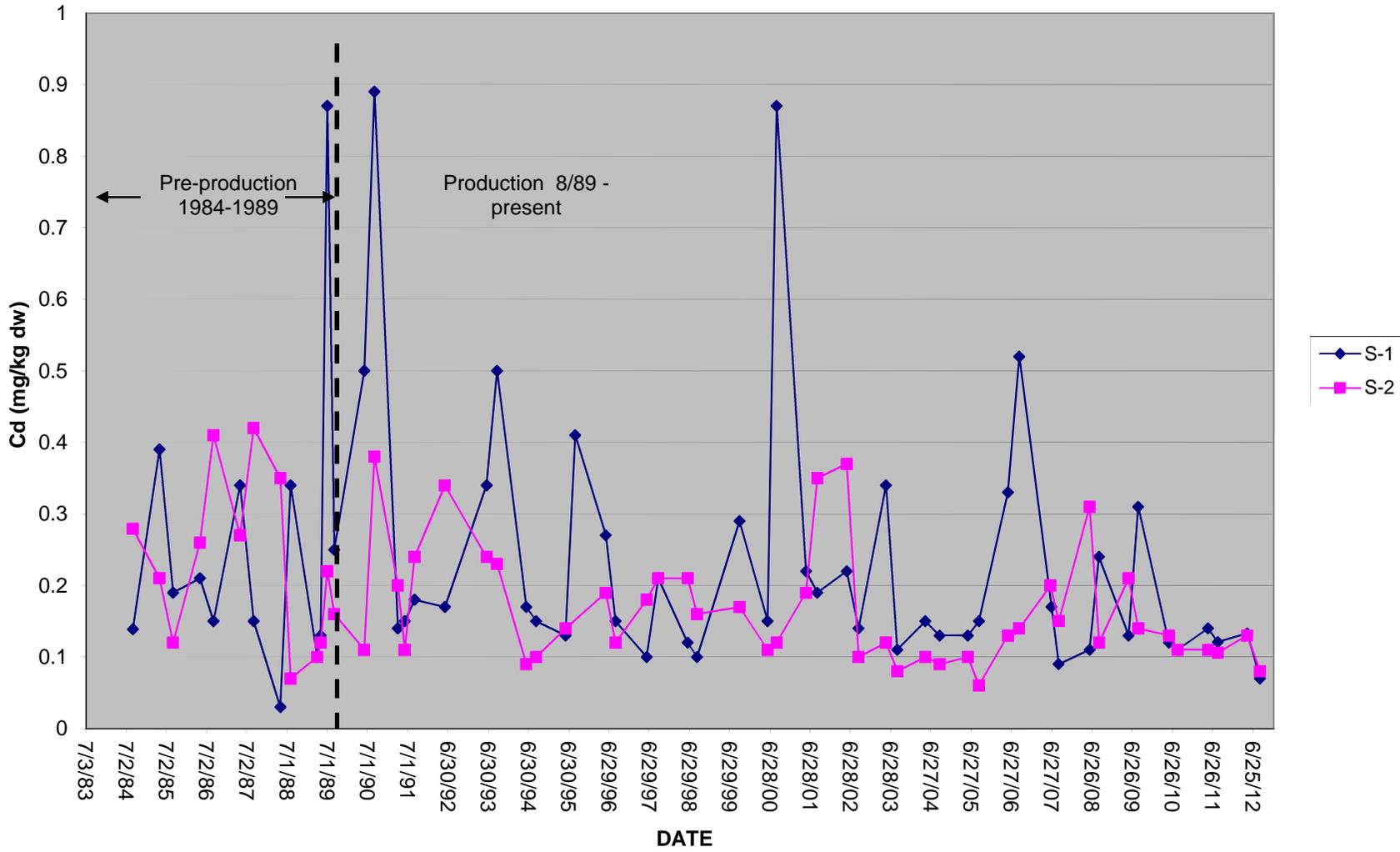


FIGURE 3-2

COPPER IN SEDIMENTS S-1 and S-2

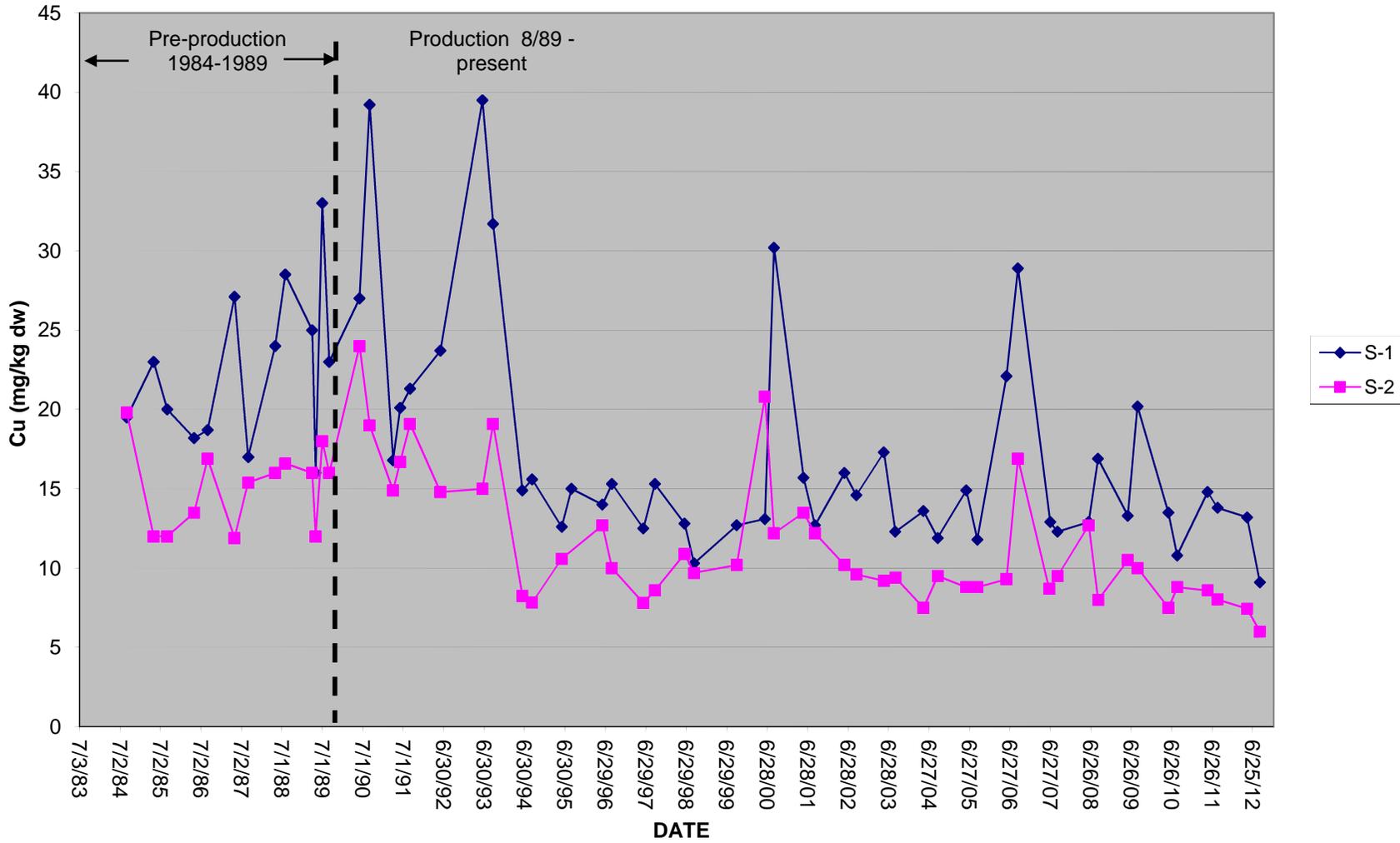


FIGURE 3-3

MERCURY IN SEDIMENTS S-1 and S-2

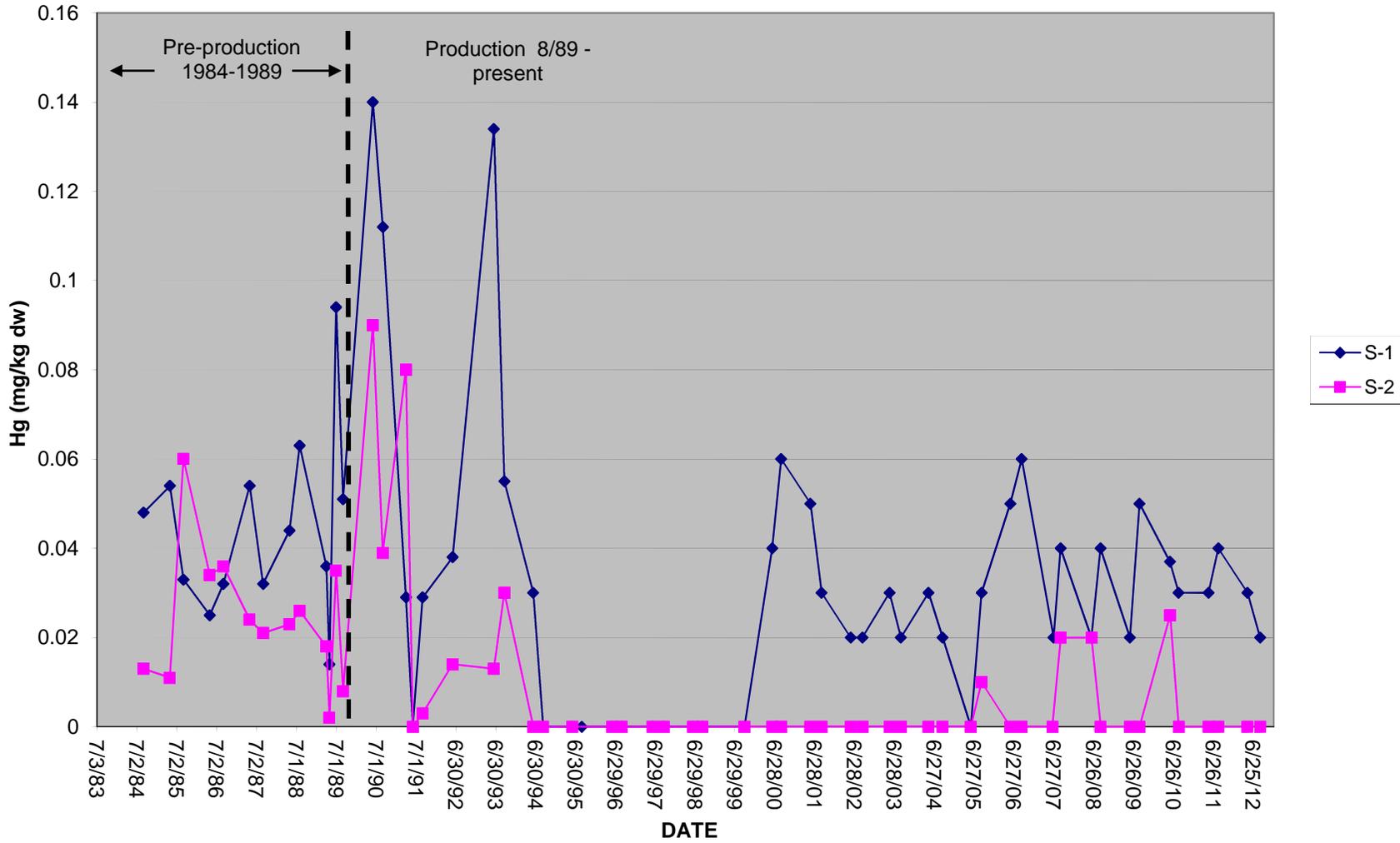


FIGURE 3-4

LEAD IN SEDIMENTS S-1 and S-2

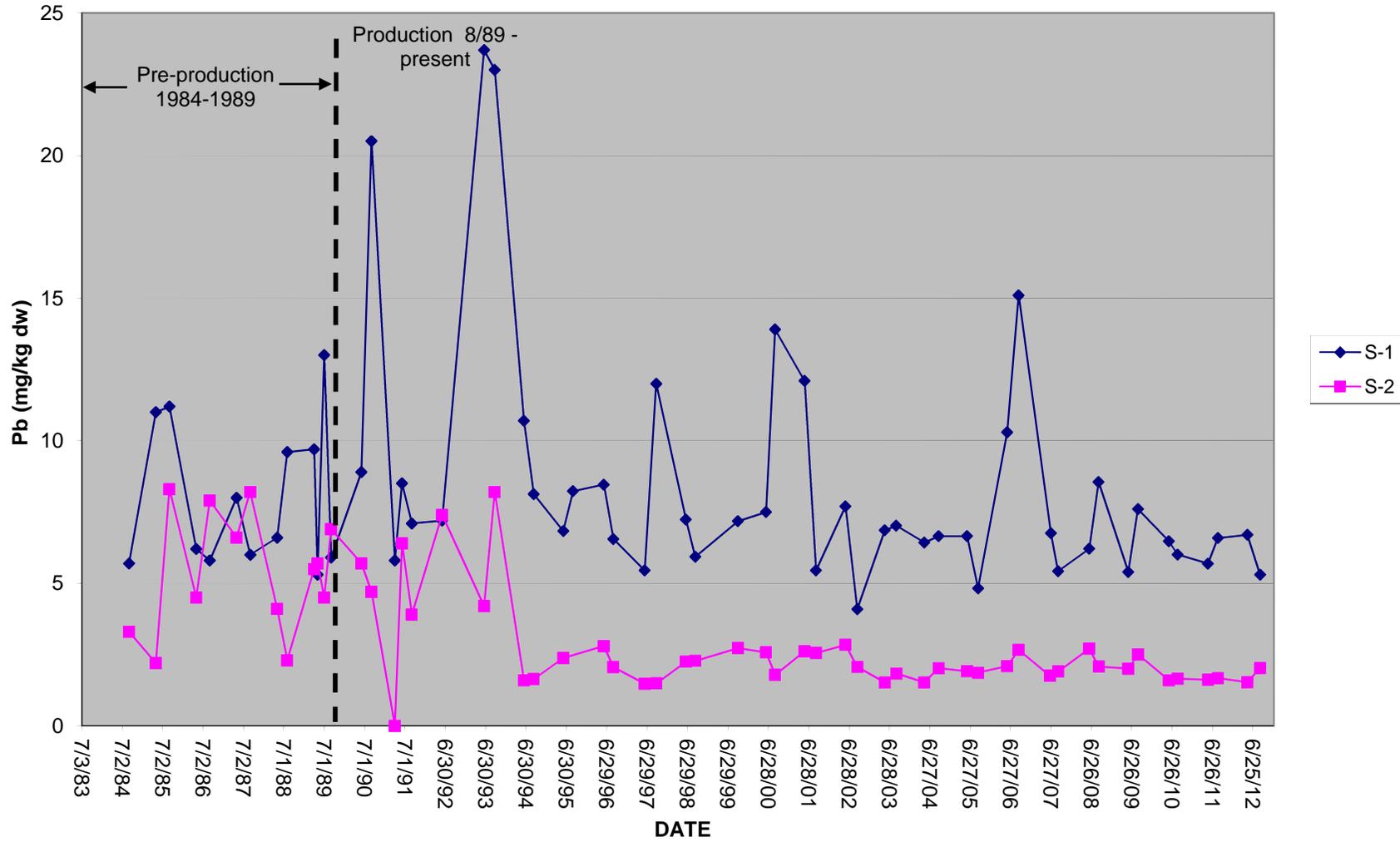


FIGURE 3-5

ZINC IN SEDIMENTS S-1 and S-2

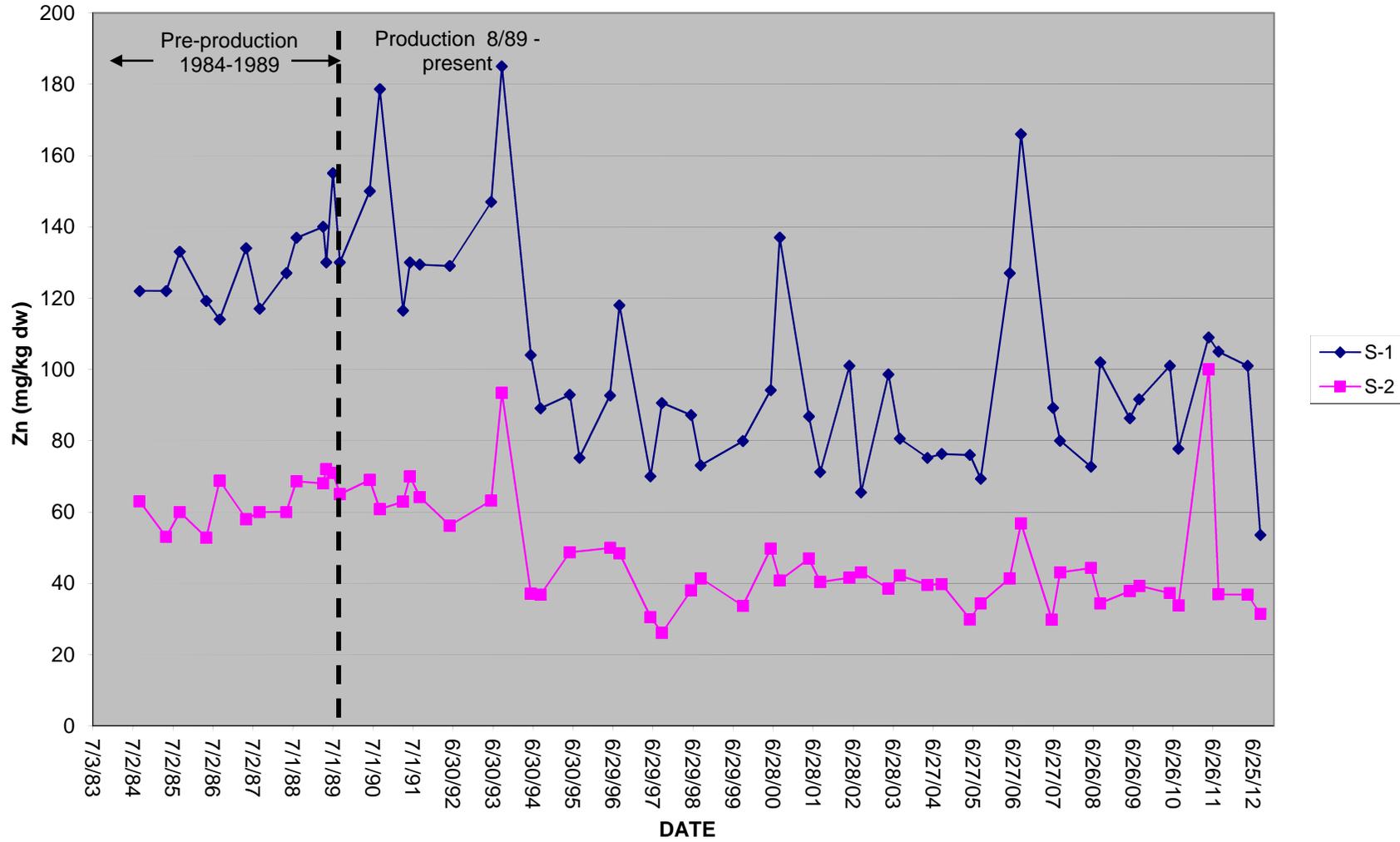


FIGURE 3-6

CADMIUM IN SEDIMENT S-4, S-5S, S-5N

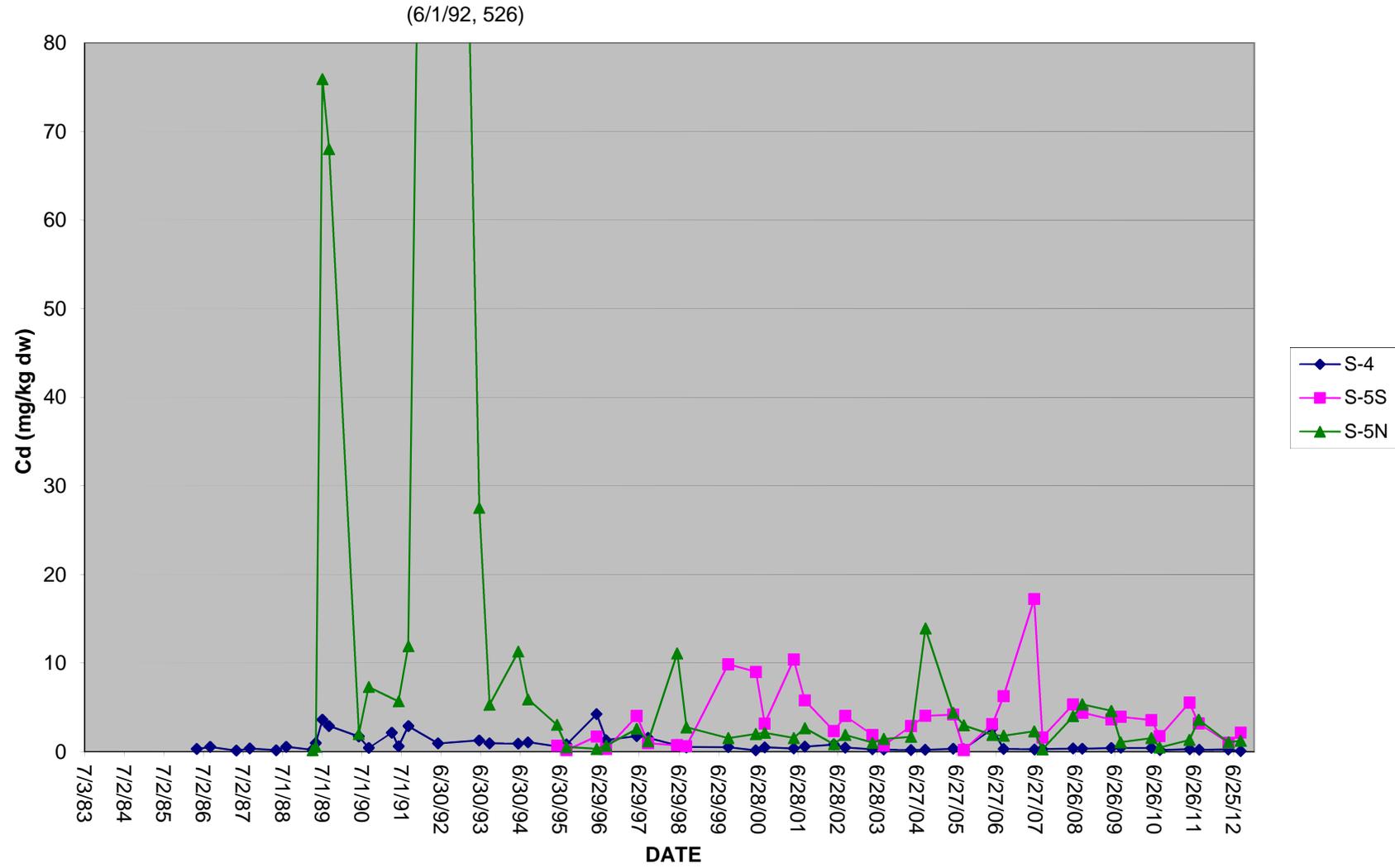


FIGURE 3-7

COPPER IN SEDIMENTS S-4, S-5N, S-5S

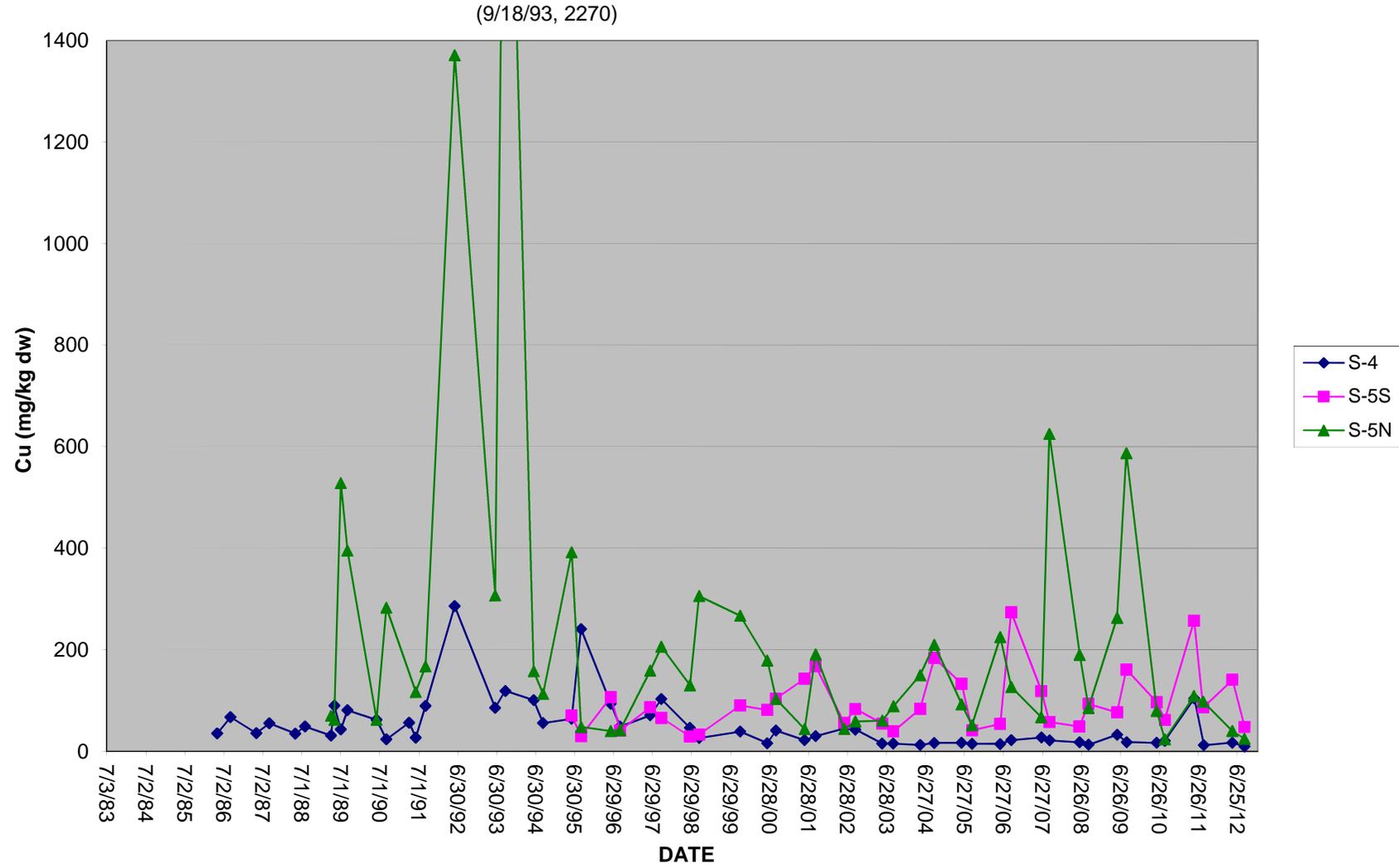


FIGURE 3-8

MERCURY IN SEDIMENTS S-4, S-5S, S-5N

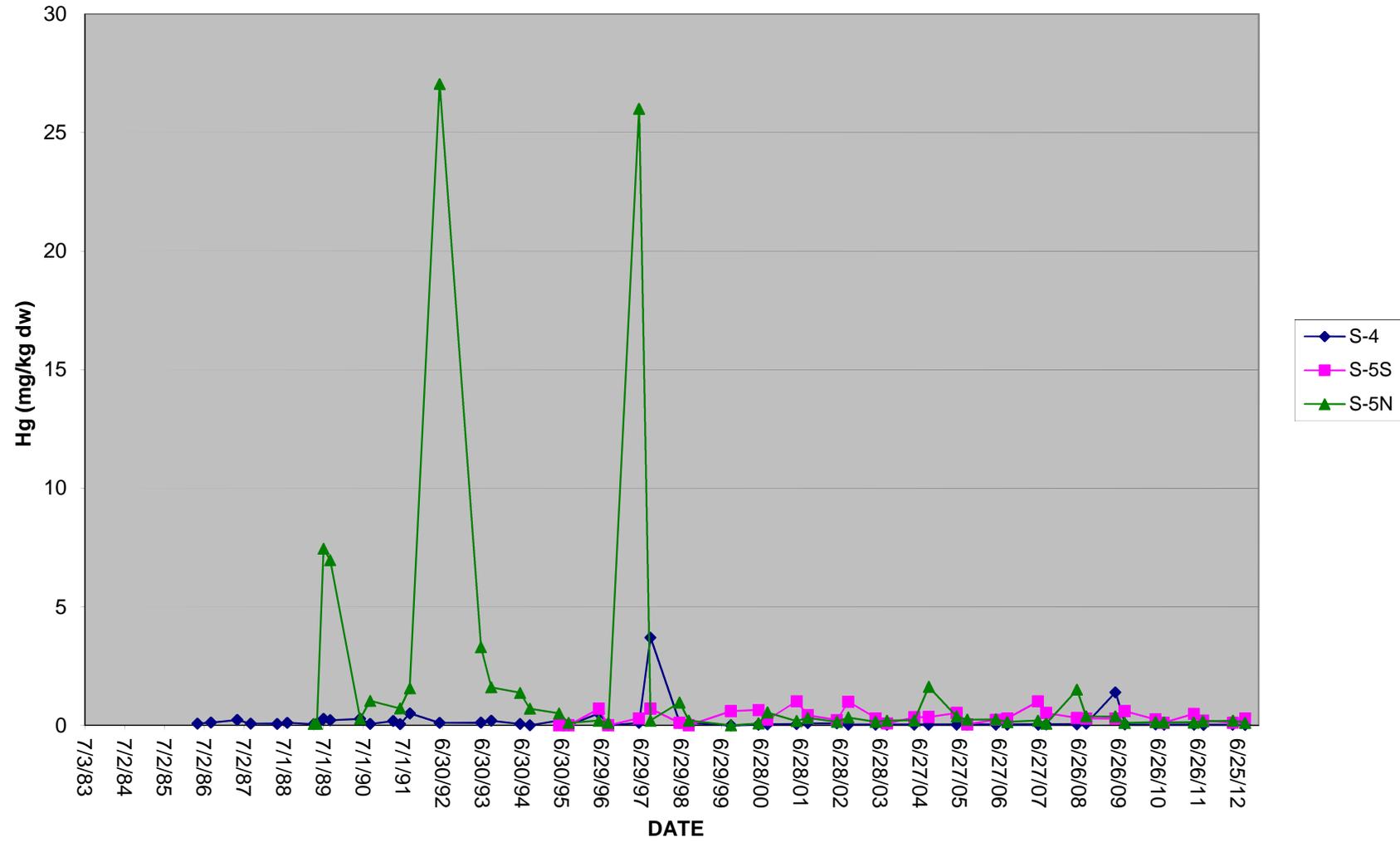


FIGURE 3-9

LEAD IN SEDIMENTS S-4, S-5S, S-5N

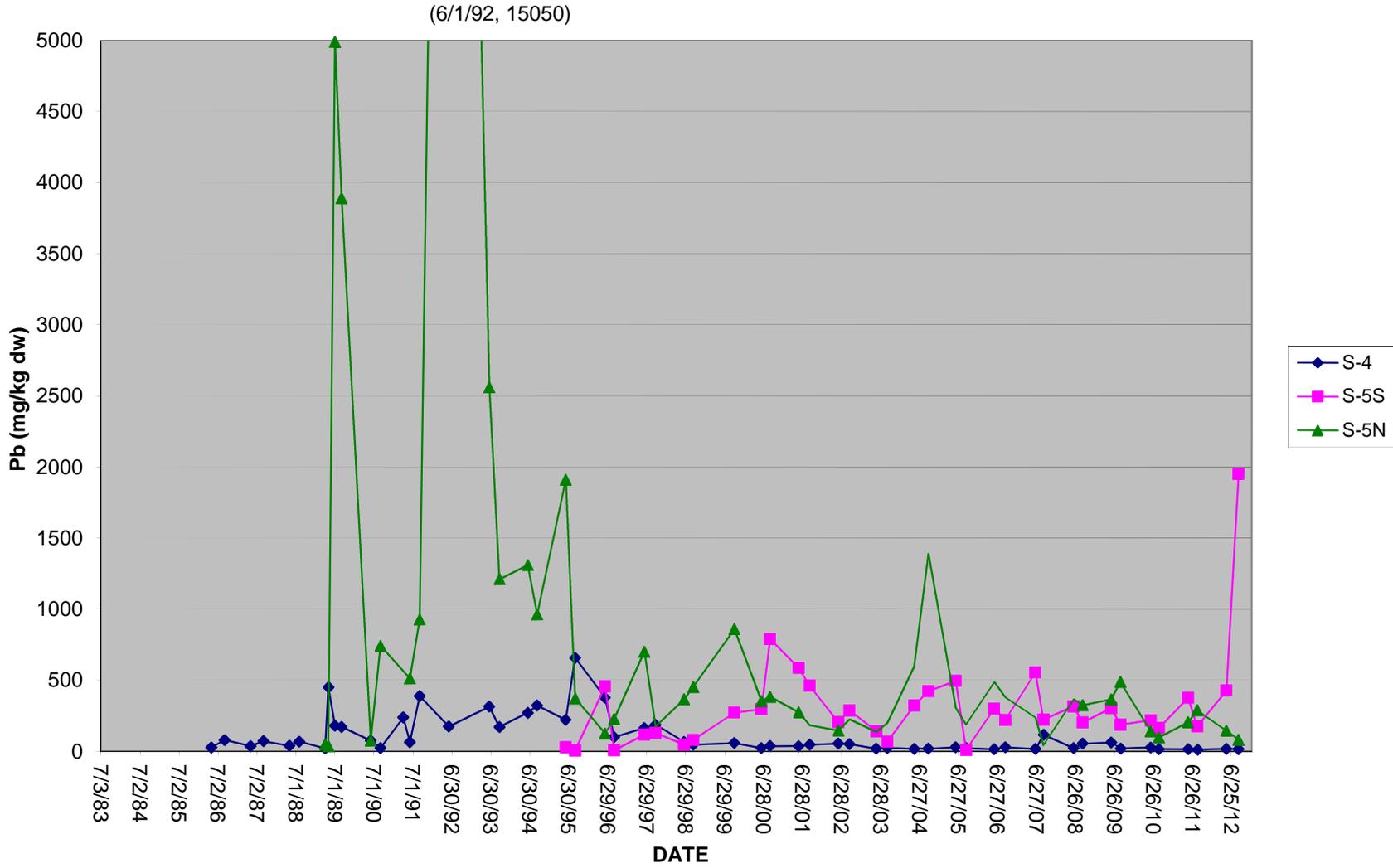


FIGURE 3-10

ZINC IN SEDIMENTS S-4, S-5S, S-5N

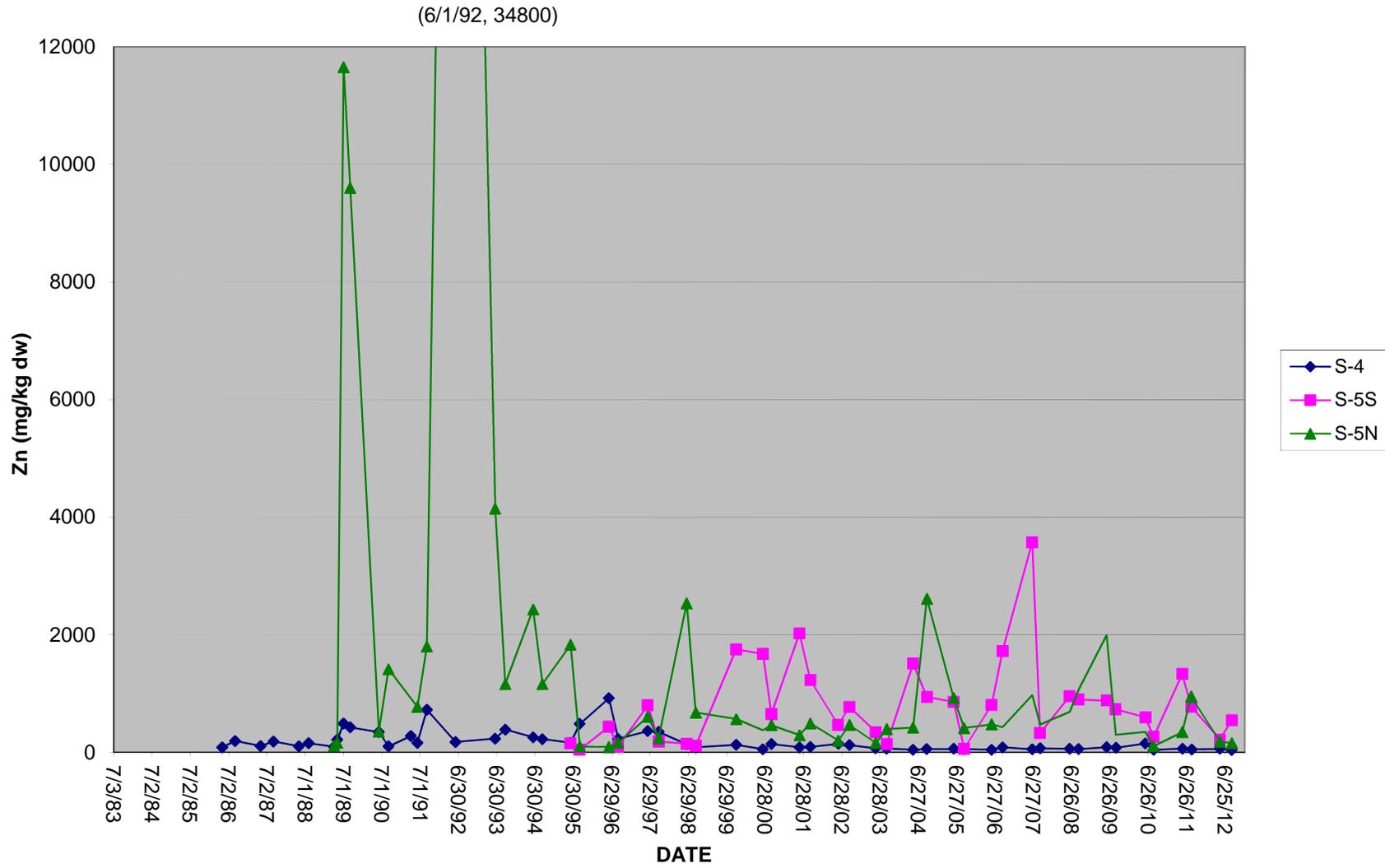


FIGURE 4-1

CADMIUM IN MUSSELS STN-1, STN-2, STN-3, ESL

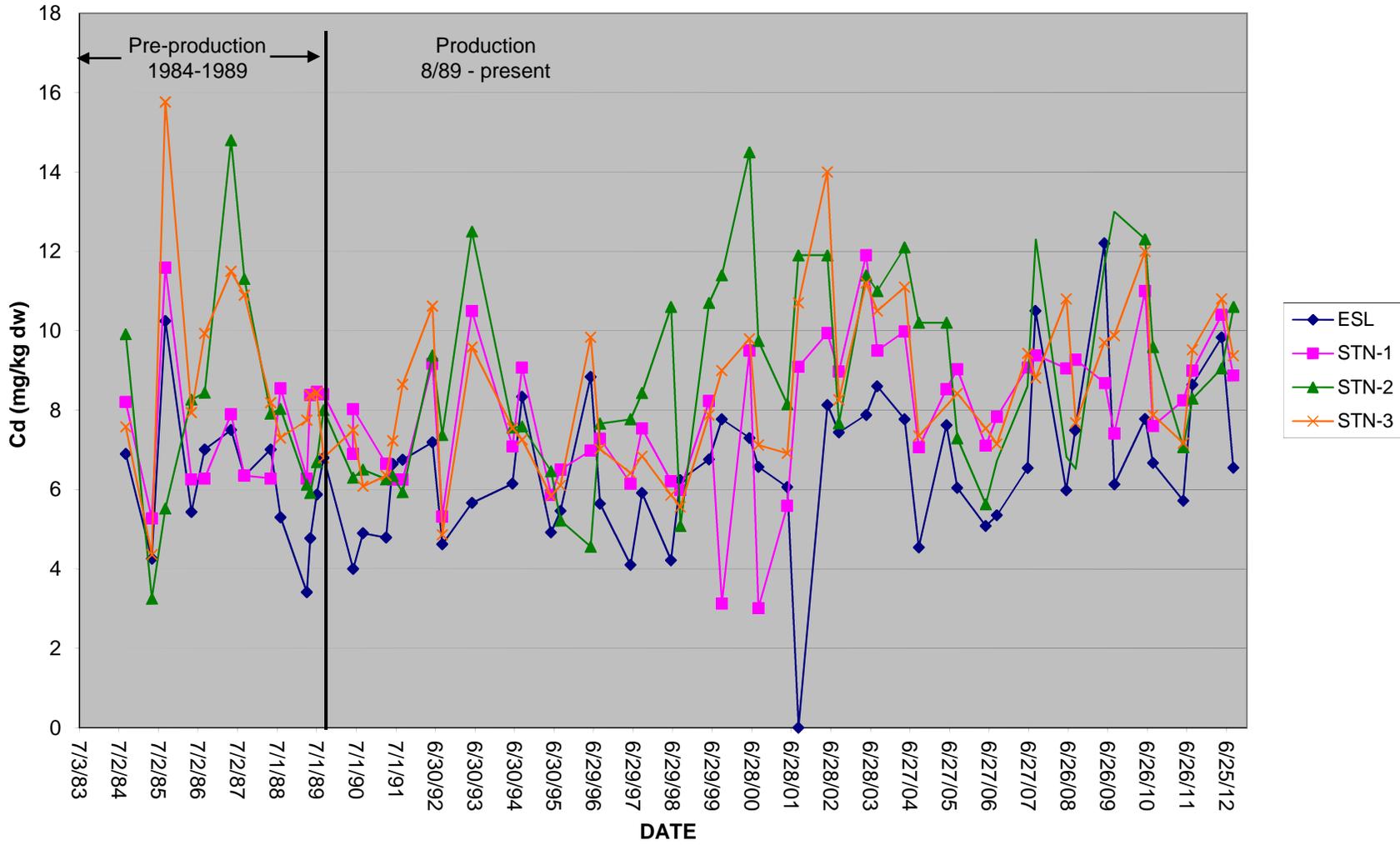


FIGURE 4-2

COPPER IN MUSSELS STN-1, STN-2, STN-3, ESL

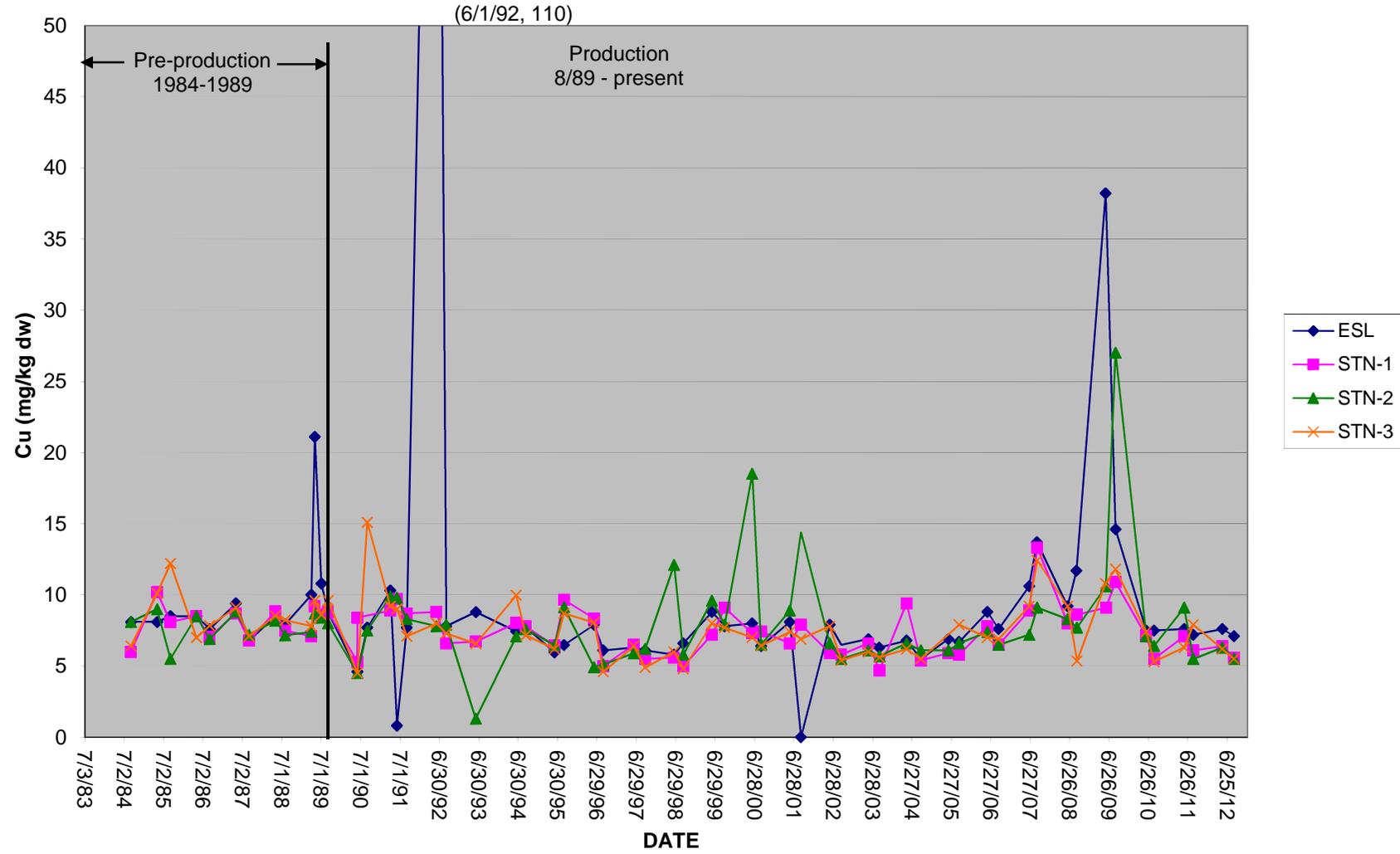


FIGURE 4-3

MERCURY IN MUSSELS STN-1, STN-2, STN-3, ESL

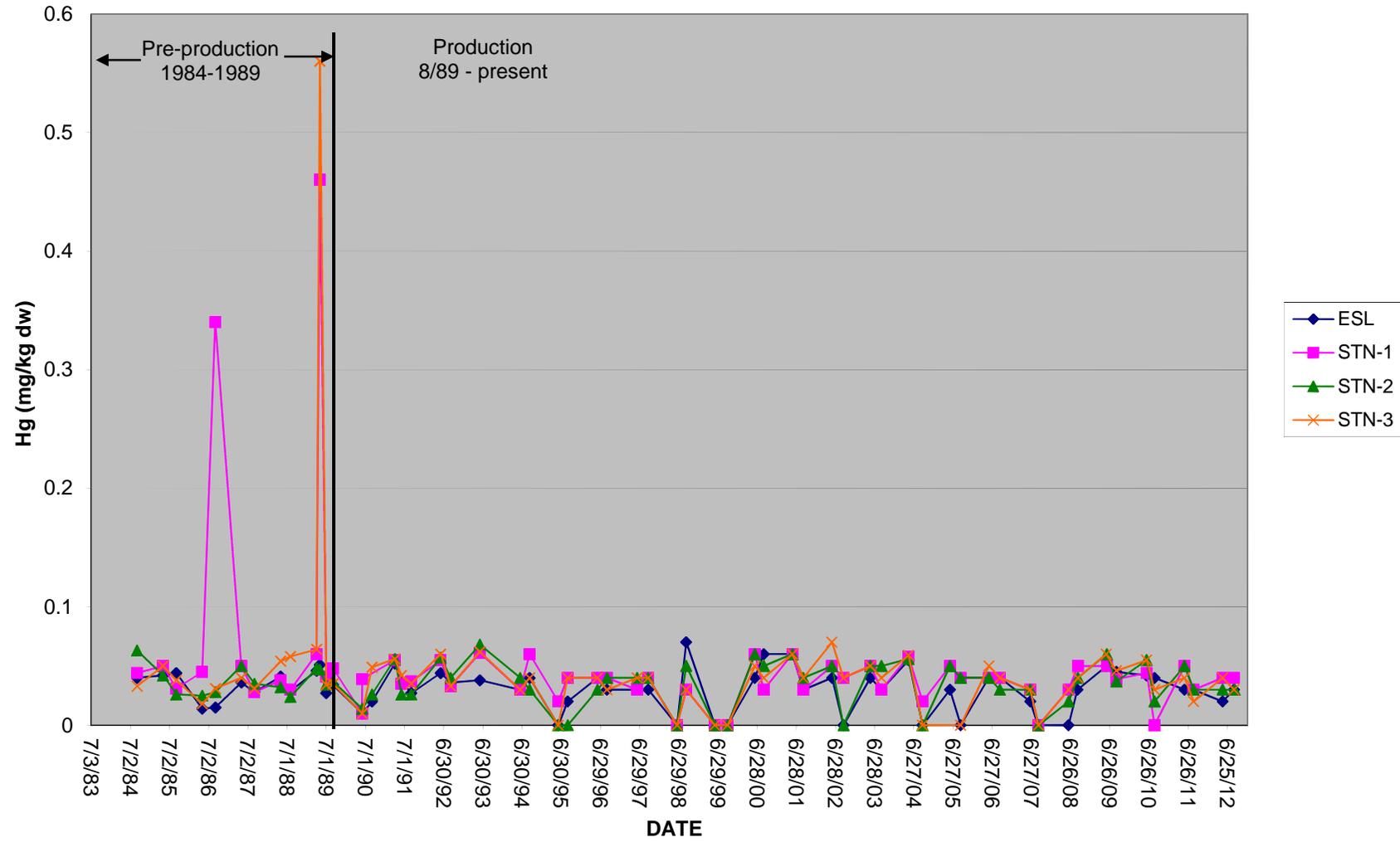


FIGURE 4-4

LEAD IN MUSSELS STN-1, STN-2, STN-3, ESL

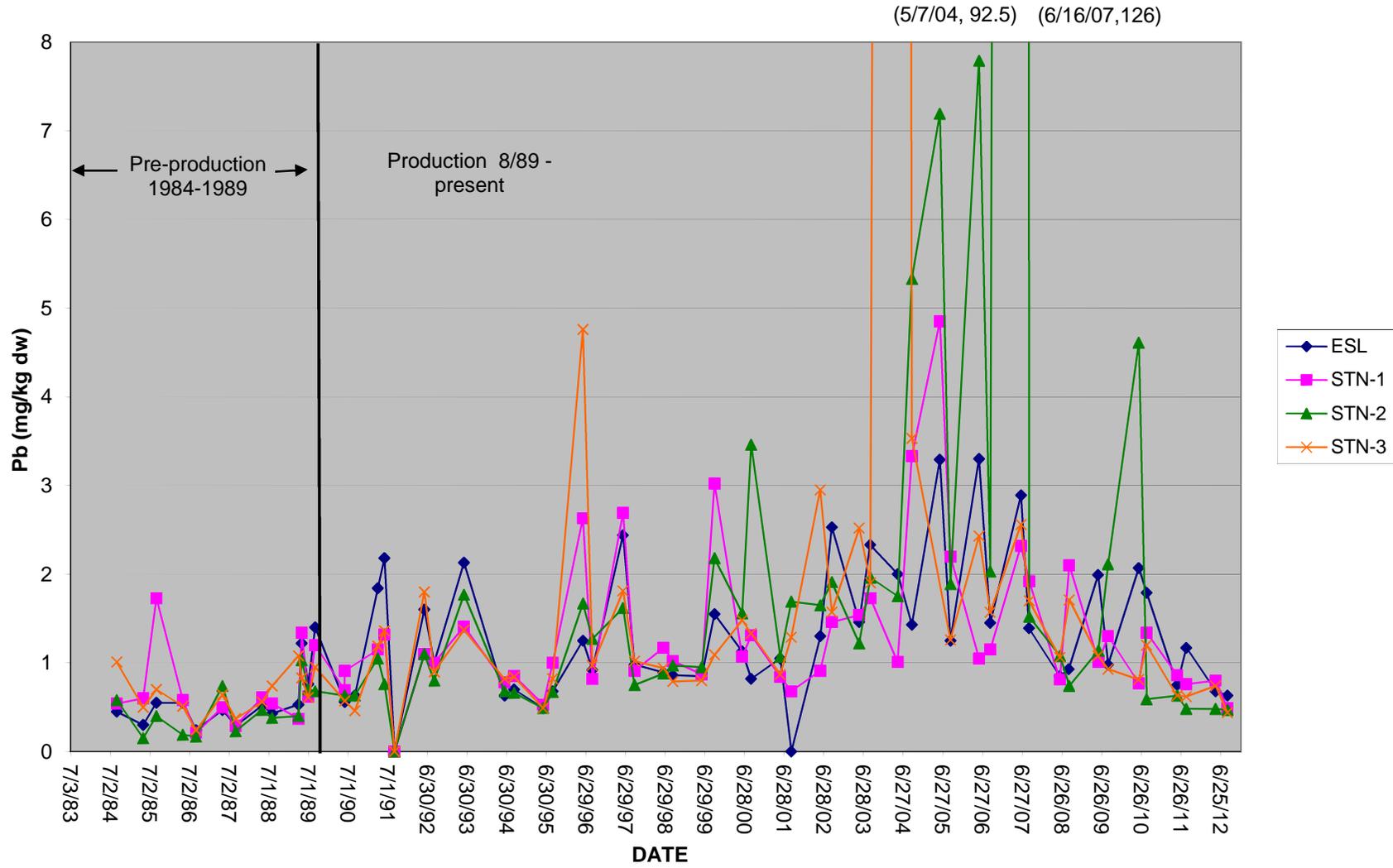


FIGURE 4-5

ZINC IN MUSSELS STN-1, STN-2, STN-3, ESL

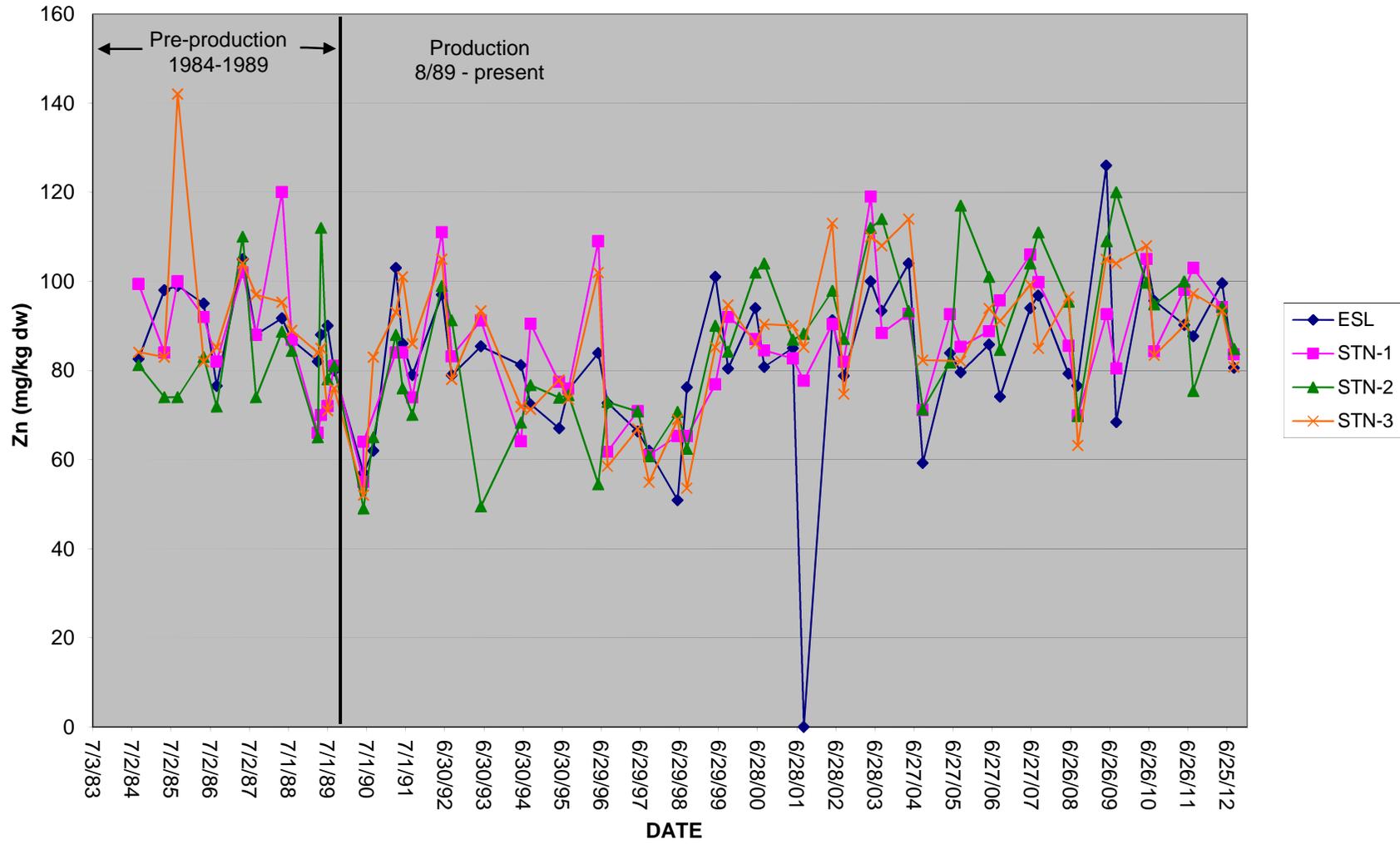


FIGURE 4-6

CADMIUM IN NEPHTYS S-1, S-2, S-4

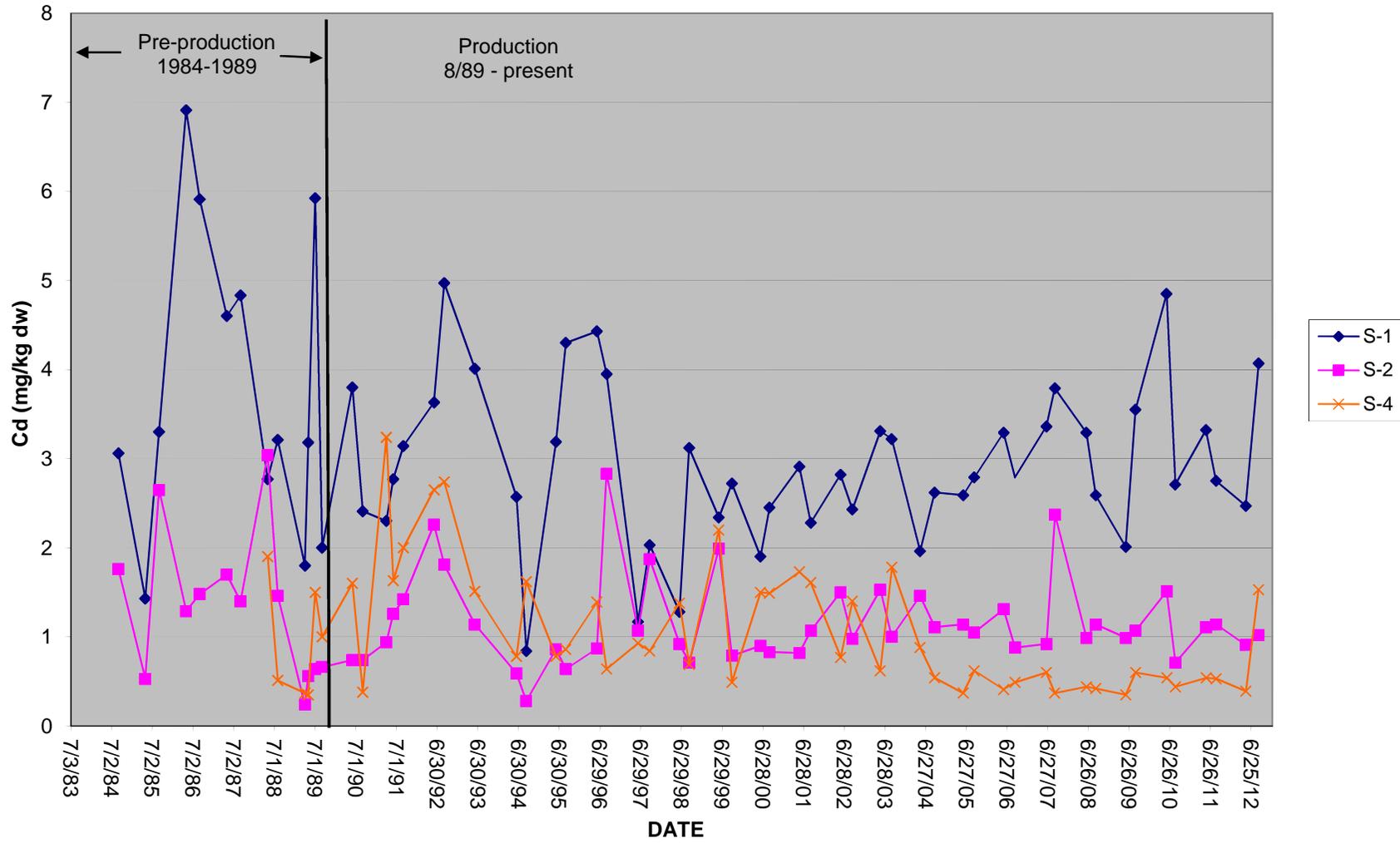


FIGURE 4-7

COPPER IN NEPHTYS S-1, S-2, S-4

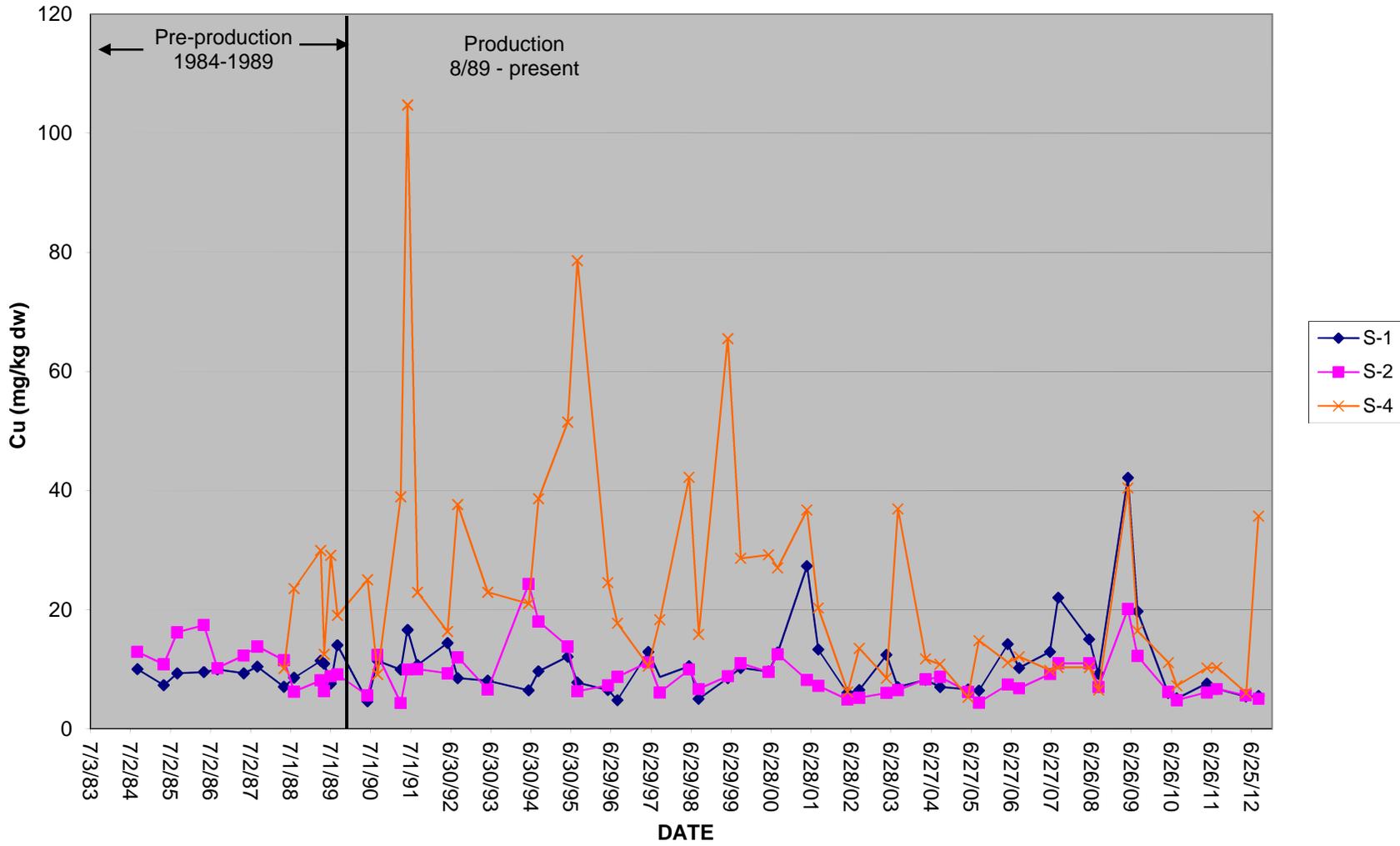


FIGURE 4-8

MERCURY IN NEPHTYS S-1, S-2, S-4

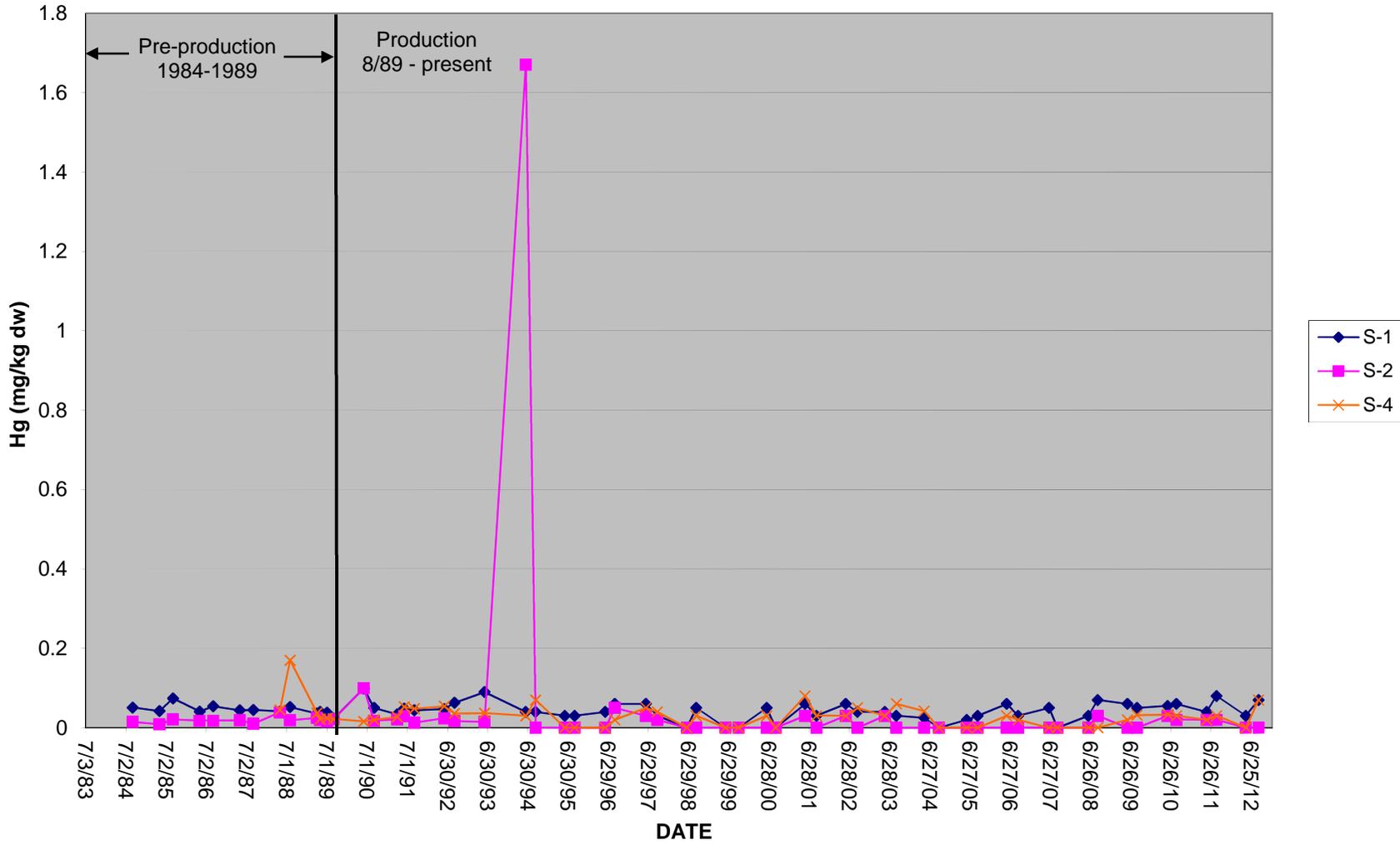


FIGURE 4-9

LEAD IN NEPHTYS S-1, S-2, S-4

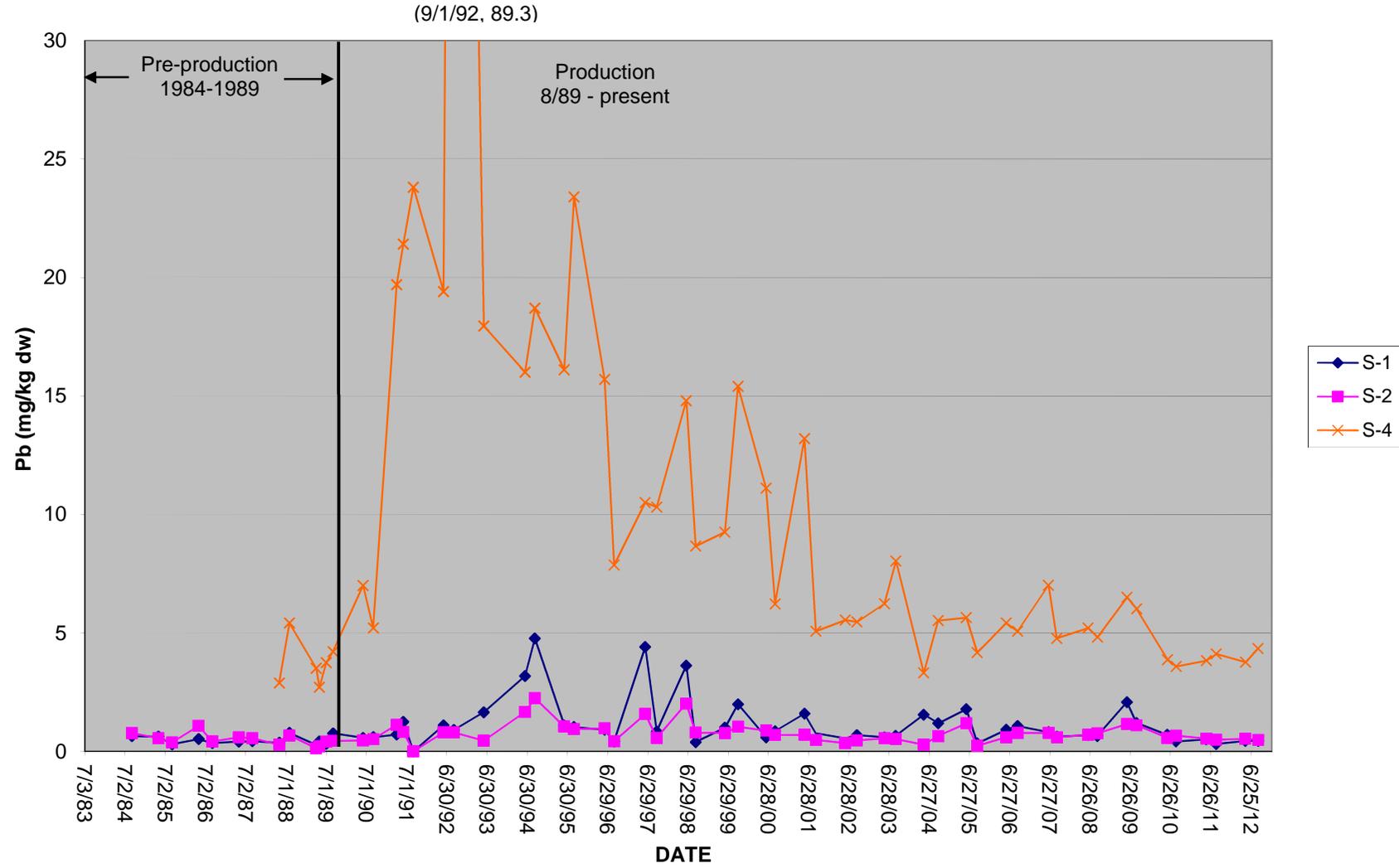
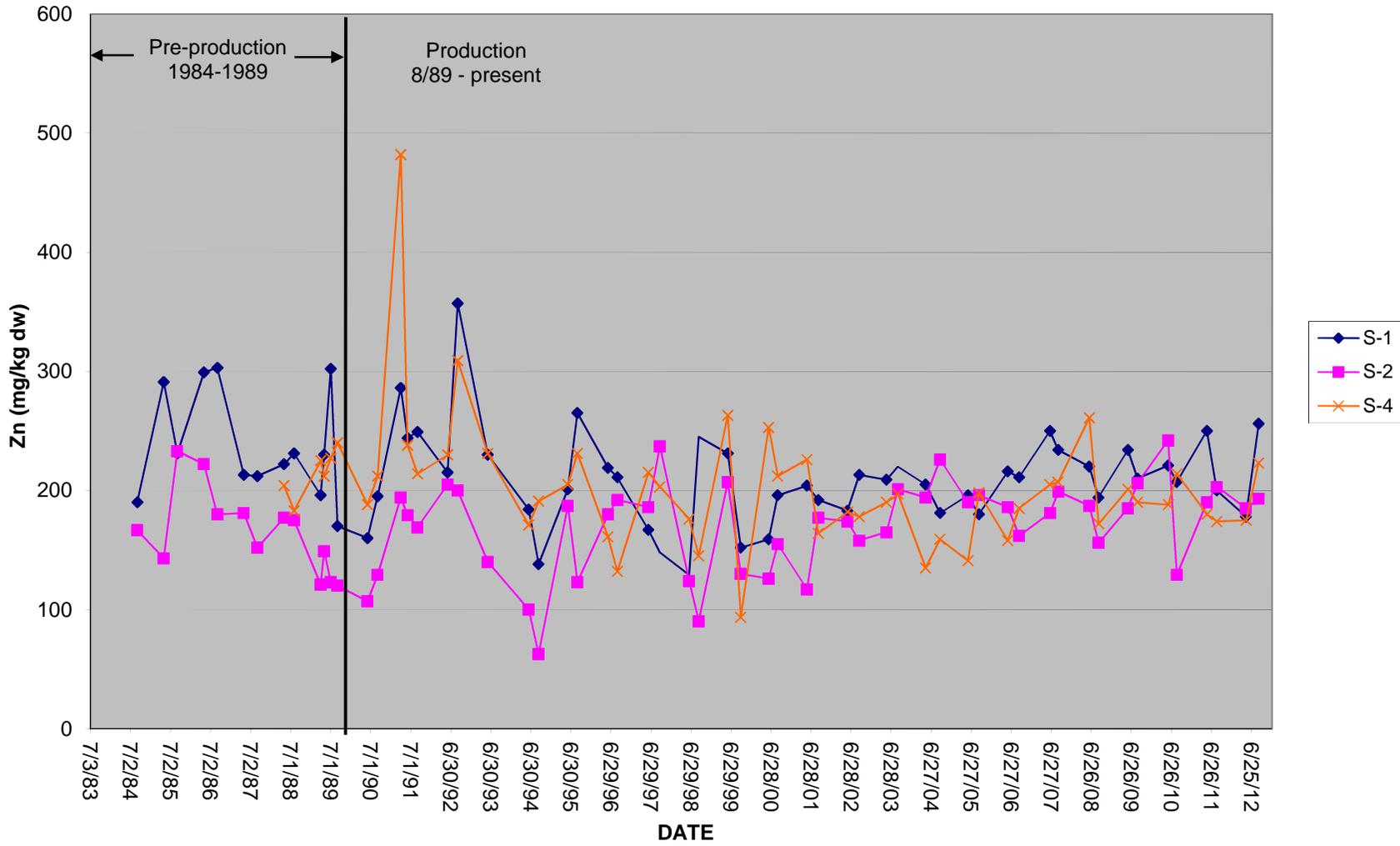


FIGURE 4-10

ZINC IN NEPHTYS S-1, S-2, S-4



Appendix A

Outfall Survey Footage CD