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Heavy Metal Concentrations in Water and Surface Sediments of Wilgreen Lake, Madison County, Kentucky

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ABSTRACT

Heavy metal pollution remains problematic in natural waters, particularly for localities near plausible anthropogenic sources. We assayed the level of heavy metals in surface waters and within surface sediments of Wilgreen Lake, whose watershed drains industrial, urban, agricultural, and residential areas near Richmond, Kentucky. Water samples were treated according to Environmental Protection Agency (EPA) protocols and digested with trace-metal-grade nitric and hydrochloric acids. Sediment samples were collected with a grab sampler and digested using established EPA procedures with hydrogen peroxide and trace-metal-grade nitric acid. Both water samples and sediment samples were sent to Activation Laboratories for analysis, and were measured via ICP/MS and ICP/OES, respectively.

All water samples had heavy metal concentrations far below the safety limit for drinking water as determined by the EPA and Kentucky Division of Water (KDW). Lead and nickel were elevated above chronic criteria for aquatic habitat as established by the KDW. Several metals lead, thorium, and thallium showed increases in concentration in deeper, anoxic waters compared to oxygenated, surface samples, implying their diffusion out of the sediments. In surface sediments of the lake, heavy metal concentrations show no systematic increase or decrease at stations distributed across the lake. However, two stations M-2 and TF-1 located near the inflow of Taylor Fork showed considerably higher concentrations of lead, chromium, and cobalt than other grab samples. Elevated metal concentrations within sediments in the upper reaches of Taylor Fork can occur from two very different sources. Metals may have originated in the watershed from industrial sources and accumulated within sediments, or they may have entered the lake from septic systems or runoff from the residential areas.

INTRODUCTION

Wilgreen Lake's watershed drains industrial, urban, agricultural, and residential areas near Richmond, Kentucky (Fig.1) since its damming in the mid 1960's. In 2008, Borowski (personal communication) measured heavy metal concentrations within Wilgreen lake waters, finding that some metals existed at levels exceeding those recommended by the EPA (Environmental Protection Agency) and KDW (Kentucky Division of Water). (Table 1). This finding has prompted this more thorough investigation of heavy metal levels in lake waters and surface sediments with the ultimate goal of perhaps delineating heavy metal sources to the lake. Wilgreen Lake's watershed consists of two major streams, Taylor Fork and Old Town Branch that we assayed for any heavy metals in both water samples and surface sediments. It has a 142 acre surface water area, 13.3 kilometers of shore line, 14.6 meter maximum depth and a mean depth of 6.4 meters.

Pollutant	Exceeds EPA or KDW drinking water standards	Frequency	Exceeds KDW natural water standards	Frequency
Barium	No	---	---	---
Cadmium	No	---	Yes	7 of 7 samples
Chromium	No	---	---	---
Copper	No	---	Yes	7 of 7 samples
Lead	Yes	1 of 7 samples	Yes	4 of 7 samples
Mercury	---	---	---	---
Nickel	No	---	Yes	7 of 7 samples
Selenium	No	---	No	---

Table 1. Heavy metal concentration findings for Wilgreen Lake in 2007 relative to EPA and the KDW standards.(Borowski personal communication). (Table 1)
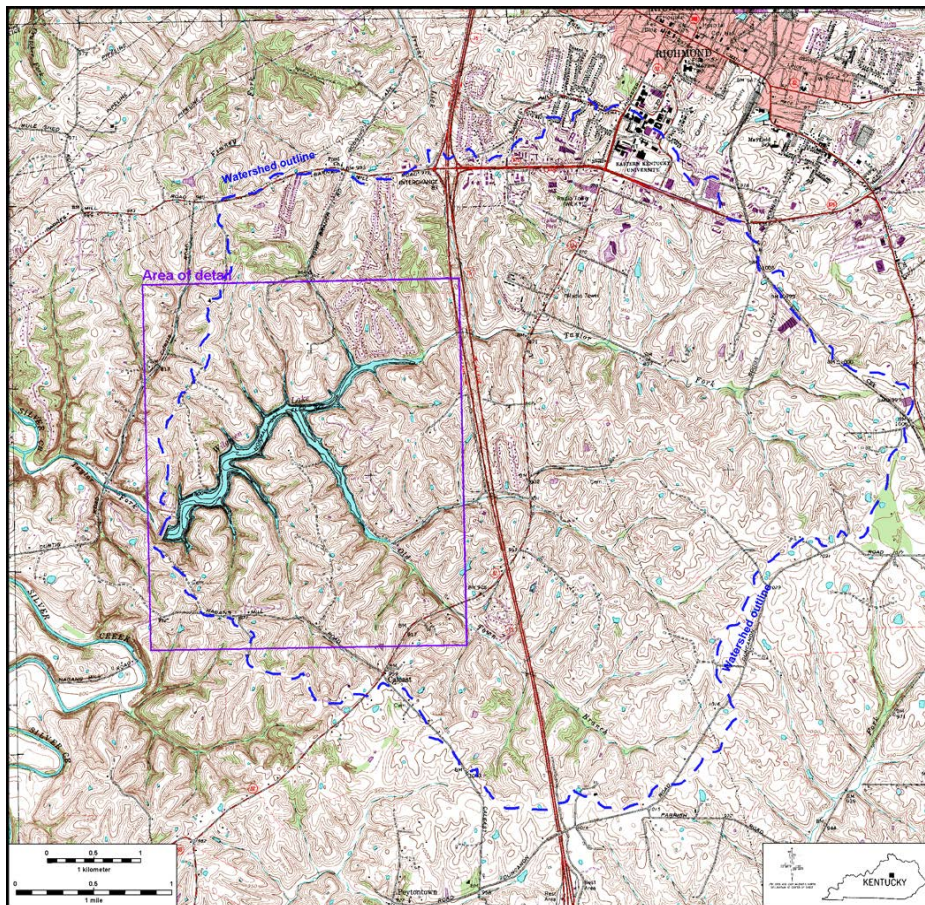
Figure 1. *Map showing Wilgreen Lake's proximity to Richmond, Ky. The rectangular*
section is the map of our research area (see Fig. 4).

Heavy metals in freshwater environments

Heavy metals have certain behavioral characteristic once introduced into
freshwater environments. Heavy metals can be added to the lake dissolved within stream
water, as particulates that settle from the atmosphere, or absorbed onto sediment
particles/organic molecules. Once these heavy metals encounter the lacustrian
environment they are incorporated into the lake sediment. Once sequestered in sediments,
metals, may not permanently reside there. Heavy metals in the sediment may re-enter the
dissolved phase under certain geochemical conditions and diffuse into overlying lake
water increasing their mobility. The factors that can affect mobility are pH and oxygen
concentrations. In the absence of oxygen some heavy metals form insoluble minerals and
some heavy metals tend to gain mobility.

Lake environments are prone to anoxia both in the water column and in
sediments. High organic loading promotes anoxia in lake sediments, and eutrophic lakes
usually experience stratification and anoxia in lake waters during the summer. Once
heavy metals gain mobility and enter the water system they can either enter the water
supply or be incorporated in the tissues of organisms in a process known as

bioaccumulation. Heavy metals cannot be broken down into simpler; less toxic forms so they become higher in concentration in the tissues of organisms accumulating through successive trophic levels of the food chain with the top most consumers ingesting the highest concentrations. People occupy the highest level of the trophic pyramid potentially accumulating heavy metals which can have devastating health effects. The harmful effects of these heavy metals include cancer, kidney damage, liver damage, [blood, nervous system, circulatory, bone tissue, child development complications] gastrointestinal distress, increased blood pressure, skin irritation, ulceration, hair and fingernail loss.

Wilgreen Lake stratification

Lake stratification is potentially important in heavy metal storage and release. Solar heating in the Spring and Summer creates a warm, less dense layer that rests upon a lower, colder more dense layer. A thermocline develops which creates a density boundary separating the surface layers from the bottom layers. The upper layer is well mixed with similar temperature (Fig. 2). The transition to the lower, cold layer is marked by the thermocline where temperature decreases rapidly with increasing depth. Temperature decreases at a more constant rate once passing the thermocline.

Oxygen concentration is related to thermal stratification (Fig. 1). The top layer is fully oxygenated, receiving its oxygen from the atmosphere and from photosynthesis carried out by algae and phytopklankton. Oxygen quickly decreases with depth into the lower layer of the lake. In August 2010, we observed that the lower waters of the lake

were anoxic over its entire extent (Fig. 3). Oxygen decreases in lake waters and sediments due to decomposition of organic matter. Decomposition occurs as phytoplankton bodies settle through the water column to the bottom, and within the sediments where organic matter accumulates. Decomposition or rotting reactions are carried out by microbes and the process consumes oxygen:

$$CH_2O + O_2 ---> CO_2 + H_2O$$
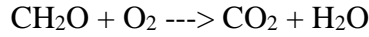
Sufficient quantities of organic matter drive lake waters and sediments to anoxia. Wilgreen sediments are generally anoxic, and lake waters typically are anoxic in the late Spring, Summer, and early Fall (Jolly and Borowski, 2007; Hunter and Borowski, 2008; Stockwell and Borowski, 2008).

The significance of the lake stratification to heavy metals is some heavy metals can mobilize under anoxic conditions when low-levels of oxygen occur, during stratification. Mobility can also occur when previously anoxic environments become oxygenated, during turnover.
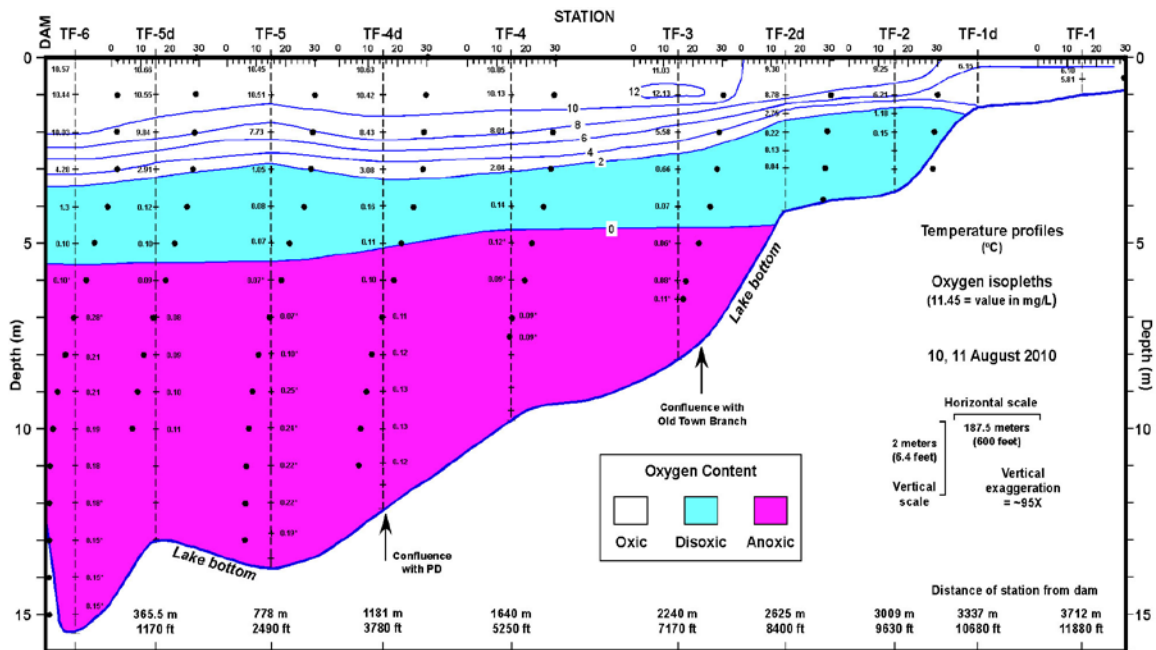
Heavy metal sources for Wilgreen Lake

Two major watersheds enter the lake, Taylor Fork and Old Town Branch. Taylor Fork is the larger stream and its watershed has industrial development that includes Sherwin Williams and Enersys. Sherwin Williams produces paint and Enersys primarily makes batteries. Both battery and paint production use many different heavy metals. Old Town Branch drains mainly residential and pasture but includes some industry, for example BTH Tool metal plating company. Residential areas such as Deacon Hills and Idyllwild are also possible heavy metal sources as they can be introduced into septic tanks which then end up in the runoff entering the lake. (Fig. 1).

Project Overview

To assay heavy metal concentrations and plausible anthropogenic sources we sampled lake waters and surface sediments throughout the lake. Surface sediment samples were taken at as shown in (Fig 4). Water samples were taken at the lake's surface and from deeper water to test for any correlation with oxygen levels and heavy metal diffusion from sediments. We sampled the entire water column at station TF-3 due to its close location to the affluence of Taylor Fork and Old Town Branch (Fig. 4).
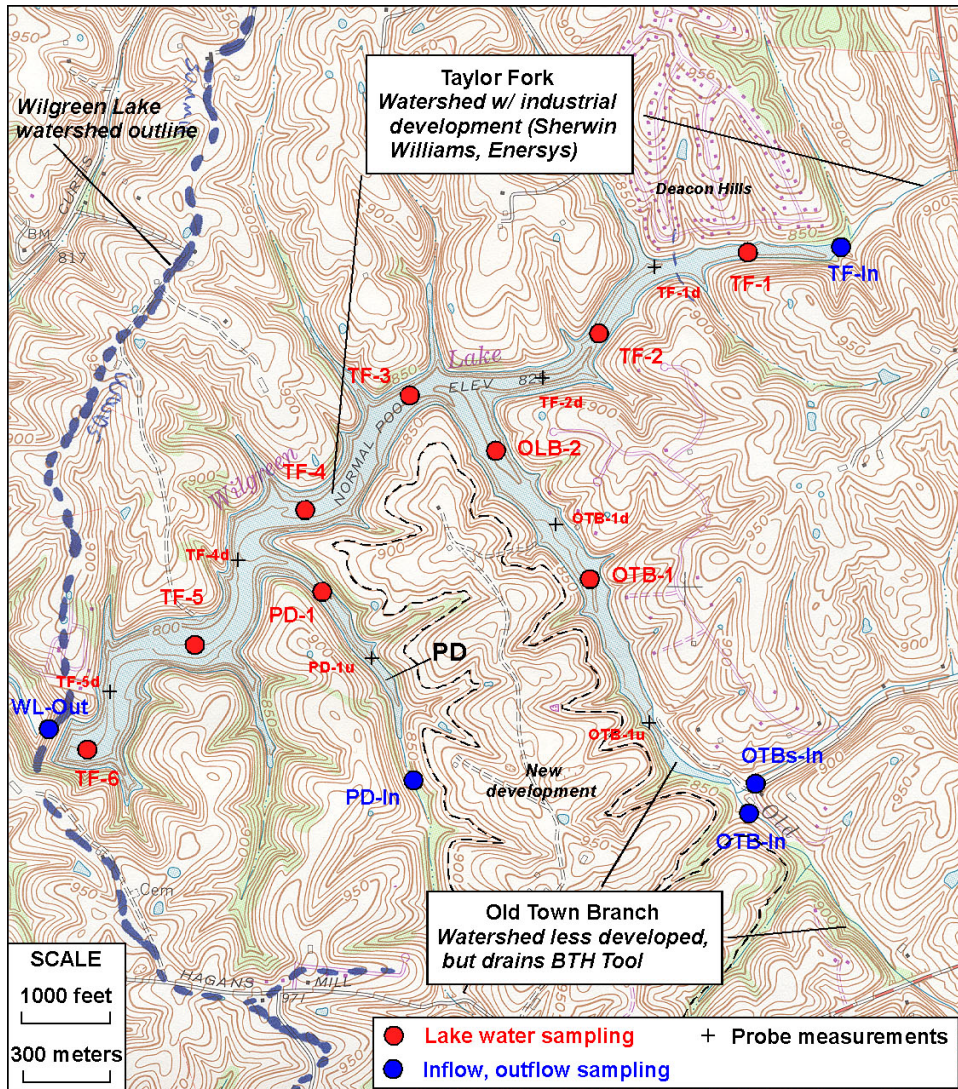
Figure 4. *Map of Wilgreen Lake sampling stations. Water samples were taken at stations denoted by filled circles. Surface sediments were also taken indicated by crosses (+). The large circle indicates station TF-3 where the full water column was sampled.*

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METHODS

Investigations on Wilgreen Lake during the 2010 field season included framework measurements (temperature, oxygen, conductivity, and pH) taken with a YSI(model 356 MPS probe), nutrient (ammonium, NH_4^+; nitrate, NO_3^-; and phosphate, PO_4^-) assays of lake waters, and sampling of both lake waters and sediments for heavy metal content (Table 2).

Water Samples

Water samples were collected according to the protocol outlined by the EPA method 200.8 (1994). Samples were unfiltered and were taken on the 10th and 11th of August 2010 (Table. 2). Polyethylene, 300-mL bottles were pre-rinsed with 2% trace-metal-grade nitric acid to remove contaminants. We took paired surface and deep samples at most stations to test the role of anoxia in mobilizing trace metals. At station TF-3, we took samples through the entire water column at 1 meter intervals. Surface samples were taken by dipping containers directly into lake water; samples at depth were taken using a Van Horn sampler (Fig. 5). Water samples were acidified to a pH more

Date	Sampling Activity
June 21, 2010	Grab sampling, water sampling, and probe measurements.
July 19, 2010	Water samples for dissolved and suspended metals.
August 10 and 11, 2010	Water samples for dissolved and suspended metals.

Table 2. Sampling activity for 2010 season.

acidic than 2 (EPA Method 200.8,1994) by adding one drop of concentrated, trace-metal-grade nitric acid to each 15 mL of sample (~20 drops per sample bottle).

Water samples were prepared for trace-metal analysis by following EPA Method 200.8 (1994), using double-distilled water and trace-metal-grade nitric and hydrochloric acids. A HotBlock heating apparatus was used for heating the digestion tubes with reflux caps supplied from Environmental Express. Digested samples were filtered within the digestion tubes using a FilterMate filter press apparatus (Environmental Express, 2010). Sealed digestion tubes were sent to Activation Laboratories for trace metal analysis via ICP/MS (Inductively Coupled Plasma / Mass Spectroscopy). We prepared method blanks to test for addition of analytes from double-distilled water and reagents. Several duplicate samples were analyzed to test for precision and accuracy.

Figure 5. Van Dorn sampler (left) and grab sampler (right).

Sediment Samples

Sediment samples were collected according to protocol outlined by EPA Method 3050 (1996). We collected surface sediments throughout the lake for heavy metal concentrations, using a grab sampler (Fig. 5).

We followed the EPA digestion procedure of Method 3050B (1996), using double-distilled water and trace-metal-grade nitric acid and hydrogen peroxide. A HotBlock heating apparatus was used for heating digestion tubes with reflux caps supplied from Environmental Express. Digested sediment samples were filtered within the digestion tubes using a FilterMate filter press apparatus (Environmental Express, 2010). Sealed digestion tubes were sent to Activation Laboratories for trace metal analysis via ICP/OES (Inductively Coupled Plasma / Optical Emission Spectroscopy). We prepared method blanks to test for the addition of analytes from double-distilled water and reagents. Several duplicate samples were analyzed to test for precision and accuracy.

RESULTS

Results of heavy metal analysis are tabulated in the appendix for both water samples and sediment samples.

Water samples

Results of the heavy metal analyses from the lake water column are tabulated in Table 3. Only 2 lead and nickel exceeded KDW (Kentucky Department of Water) heavy metal concentrations for natural water standards.

Pollutant	Exceeds KDW natural water standards	Frequency
Barium	No	---
Cadmium	No	---
Chromium	No	---
Copper	No	---
Lead	Yes	9of 24 samples
Mercury	No	---
Nickel	Yes	23 of 24 samples
Selenium	No	---

Table 3. *Frequency of heavy metals exceeding KDW natural water standards.*

Many of the heavy metals tested didn't reveal any major concentrations above water quality standards set forth by the EPA (Environmental Protection Agency).

Heavy metals in water samples exhibit 3 distinct patterns. Some elements

…..have concentrations at or barely above the method blank. Other elements antimony,

arsenic, cadmium, and chromium show little variation with depth or within oxic versus

anoxic samples. Lead, thallium, and thorium showed higher concentrations with anoxic
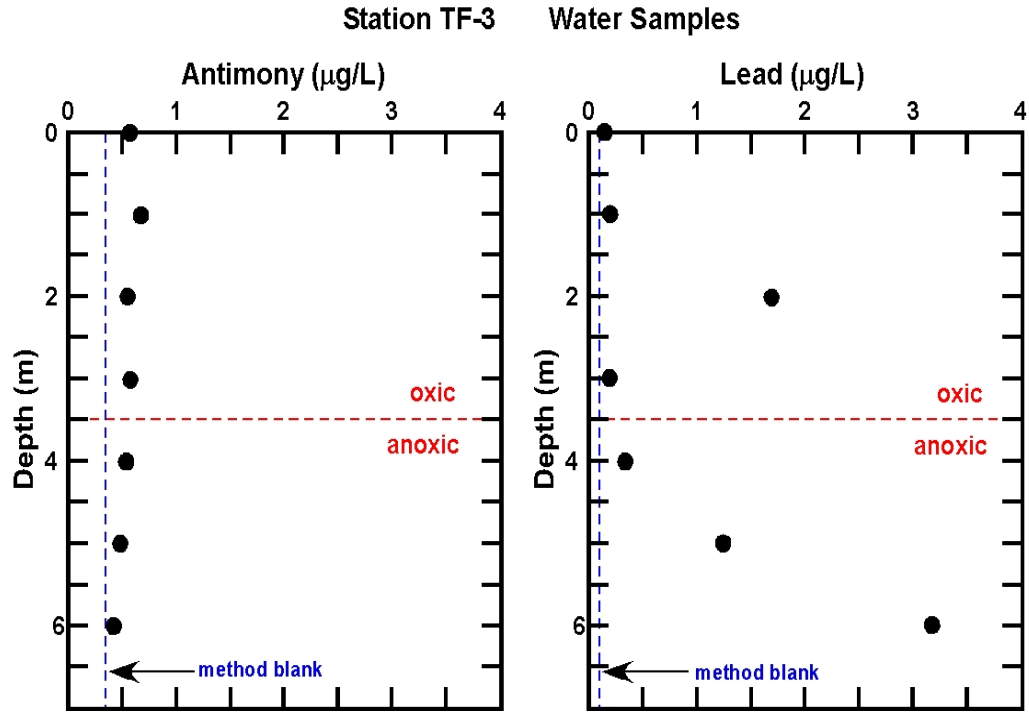
waters.

Figure 6. *Metals within the water column either show little to no variation with depth (left), or show increased concentration in deep waters associated with anoxia (right). Refer to Figure A-2 in the Appendix.*

Sediment samples

We analyzed sediment samples laterally for variation in metal concentration at each of our sampling stations in Taylor Fork, Old Town Branch, and Pond Creek. Most heavy metals arsenic, cadmium, selenium, thallium, and thorium showed little variation at these stations. Lead, chromium and cobalt at stations M2 and TF-1 in Taylor Fork shared markedly higher concentrations. (Fig. F). Refer to Figure A-1 in appendix.
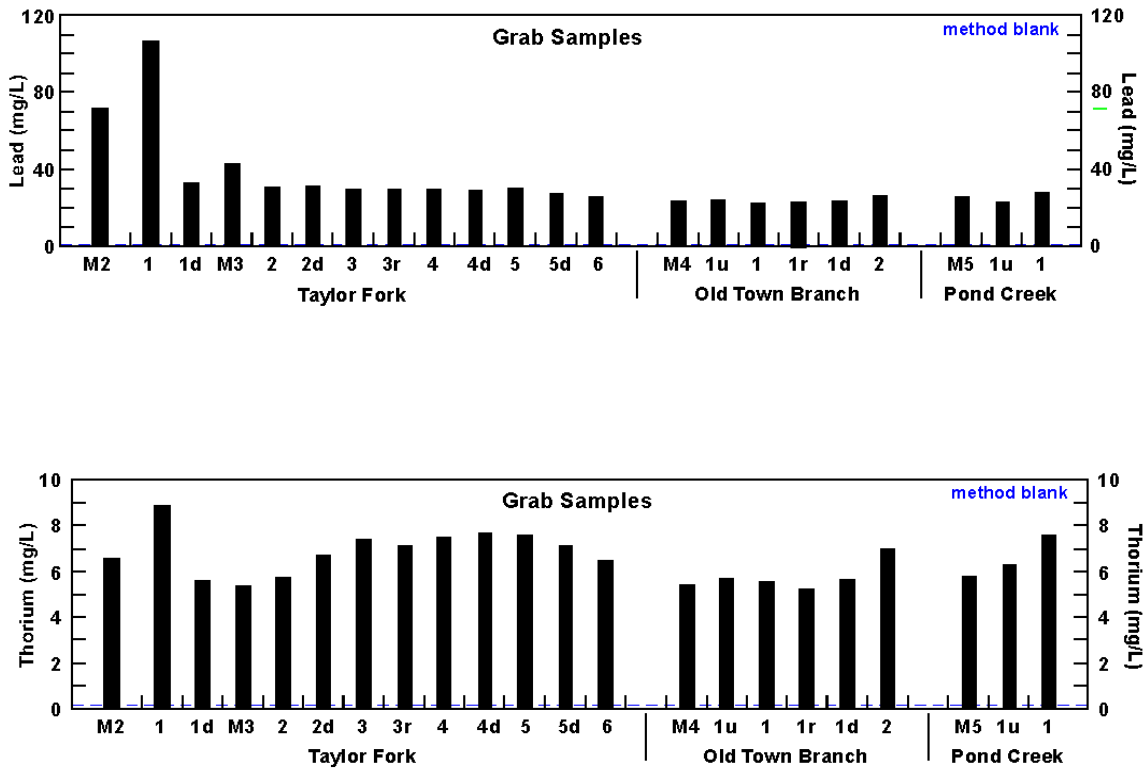
Figure 7. Lateral variation of heavy metal concentration at sampling sections of Wilgreen Lake. The concentration of the method blank is shown with a dashed line.

INTERPRETATION

Most water samples show no concentration differences in anoxic versus oxic waters, however lead, thorium, and thallium increase in concentration in the deeper, anoxic waters of Station TF-3 (Fig. 6, Fig. A-1). We infer that these elements are diffusing out of the sediments, where they occur in parts-per-million concentrations. We also surmise that these elements become mobile due to anoxia occurring in both the sediment pore waters and in the overlying anoxic lake water. The occurrence of this behavior at station TF-3 suggests that the original source(s) of these heavy metals are related to transport from the watershed and deposition of sediment within the upper reaches of Taylor Fork.

As for surface sediment samples we discovered elevated levels of lead, cobalt, and chromium suggesting possible input from stream water or septic tank effluent. Once heavy metals are introduced into surface sediment samples they can gain mobility and be injected into the water column, possibly into organisms. All sources of elevated heavy metal concentrations above KDW (Kentucky Department of Water) standards are most likely from anthropogenic sources although direct evidence of the true source area would require further study.

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USGS 7.5 minute quadrangle topographic map series, Richmond South (37084-F3-TF-024), 1965. Photorevised in 1987.

APPENDIX

Table A-1. *Trace metal concentration data for water samples taken in Wilgreen Lake.*

Depth(m)		Antimony	Arsenic	Barium	Cadmium	Chromium	Cobalt	Copper
		mg/l						
Blank		0.39	0.03	0.1	<0.01	< 0.5	0.013	3.6
TF-in		0.6	< 0.03	47.9	0.03	< 0.5	0.116	2.3
TF-1	0	0.6	< 0.03	35.8	0.03	< 0.5	0.513	2.6
TF-2	0	0.6	< 0.03	16.7	0.02	< 0.5	0.184	2.9
TF-2	2.75	0.52	< 0.03	101	0.11	< 0.5	0.475	2.2
TF-3	0	0.57	< 0.03	15.5	0.01	< 0.5	0.142	1.6
TF-3	1	0.67	< 0.03	34.8	0.02	< 0.5	0.119	1.8
TF-3	2	0.55	< 0.03	16.2	0.02	< 0.5	0.08	1.7
TF-3	3	0.58	< 0.03	29.1	0.02	< 0.5	0.075	1.7
TF-3	4	0.54	< 0.03	17.7	0.02	< 0.5	0.313	1.9
TF-3	5	0.49	< 0.03	24.4	0.03	< 0.5	0.908	2.2
TF-3	6	0.43	< 0.03	18.3	0.03	< 0.5	1.49	2.2
TF-4	0	0.55	< 0.03	22.4	0.07	< 0.5	0.097	1.8
TF-4	7.5	0.43	< 0.03	33.9	0.03	< 0.5	0.734	1.5
TF-5	0	0.65	< 0.03	28.8	0.02	< 0.5	0.084	1.6
TF-5	12	0.55	< 0.03	20.8	0.06	< 0.5	0.308	1.3
TF-6	0	0.61	< 0.03	27.1	0.03	< 0.5	0.071	1.8
TF-6	14	0.46	< 0.03	14.5	0.03	< 0.5	0.293	1.5
OTB-in		0.52	< 0.03	33.9	0.02	< 0.5	0.232	3.3
m4	0	0.57	< 0.03	28.8	0.04	< 0.5	0.456	2.4
OTB-1	0	0.57	< 0.03	20.8	0.02	< 0.5	0.541	2.7
OTB-1	1	0.71	< 0.03	27.1	0.04	< 0.5	0.699	2.6
OTB-2	0	0.64	< 0.03	14.5	0.08	< 0.5	0.137	4.2
OTB-2	5.25	0.49	< 0.03	80	0.08	< 0.5	1.08	2.4
PD-1u	0	0.59	< 0.03	15.8	0.04	< 0.5	0.124	2.2
PD-1u	3.75	0.67	< 0.03	159	0.03	< 0.5	0.726	2.3
PD-1u	3.75	0.6	< 0.03	162	0.03	< 0.5	0.776	2
PD-1	0	0.56	< 0.03	15.8	0.01	< 0.5	0.116	1.9
PD-1	6.25	0.43	< 0.03	27.4	0.03	< 0.5	0.871	1.9
PD-1	6.25	0.44	< 0.03	26.5	0.02	< 0.5	0.798	2

Table A-1. Continued

	Depth(m)	Lead mg/l	Mercury ----	Nickel	Selenium	Silver	Thallium	Thorium
blank		0.14	< 0.2	0.4	< 0.2	< 0.2	< 0.001	0.001
TF-in		0.4	< 0.2	1.2	< 0.2	< 0.2	0.01	0.018
TF-1	0	1.45	< 0.2	1.2	< 0.2	< 0.2	0.006	0.03
TF-2	0	0.48	< 0.2	1	< 0.2	< 0.2	0.002	0.011
TF-2	2.75	1.3	< 0.2	1.3	< 0.2	< 0.2	0.003	0.021
TF-3	0	0.15	< 0.2	3.2	< 0.2	< 0.2	< 0.001	0.006
TF-3	1	0.2	< 0.2	0.9	< 0.2	< 0.2	0.001	0.01
TF-3	2	1.69	< 0.2	0.8	< 0.2	< 0.2	< 0.001	0.006
TF-3	3	0.2	< 0.2	1	< 0.2	< 0.2	< 0.001	0.006
TF-3	4	0.33	< 0.2	9.7	< 0.2	< 0.2	< 0.001	0.01
TF-3	5	1.24	< 0.2	1.5	< 0.2	< 0.2	0.004	0.025
TF-3	6	3.17	< 0.2	1.2	< 0.2	< 0.2	0.004	0.032
TF-4	0	0.22	< 0.2	1.1	< 0.2	< 0.2	0.001	0.01
TF-4	7.5	1.25	< 0.2	0.8	< 0.2	< 0.2	0.001	0.013
TF-5	0	0.18	< 0.2	1.1	< 0.2	< 0.2	0.001	0.009
TF-5	12	0.32	< 0.2	1.1	< 0.2	< 0.2	< 0.001	0.01
TF-6	0	0.15	< 0.2	1	< 0.2	< 0.2	< 0.001	0.005
TF-6	14	0.23	< 0.2	2.2	< 0.2	< 0.2	< 0.001	0.003
OTB-in		0.3	0.3	1	< 0.2	< 0.2	0.007	0.008
m4	0	0.82	< 0.2	1.3	< 0.2	< 0.2	0.002	0.015
OTB-1	0	0.94	< 0.2	1.8	< 0.2	0.3	0.003	0.031
OTB-1	1	1.47	< 0.2	1.5	< 0.2	< 0.2	0.004	0.058
OTB-2	0	0.28	< 0.2	1.2	< 0.2	< 0.2	< 0.001	0.008
OTB-2	5.25	1.47	< 0.2	1.5	< 0.2	< 0.2	0.006	0.018
PD-1u	0	0.26	< 0.2	0.9	< 0.2	< 0.2	< 0.001	0.013
PD-1u	3.75	1.6	< 0.2	1.4	< 0.2	< 0.2	0.002	0.031
PD-1u	3.75	1.65	< 0.2	1.4	< 0.2	< 0.2	0.003	0.026
PD-1	0	0.19	< 0.2	0.8	< 0.2	< 0.2	< 0.001	0.006
PD-1	6.25	1.3	< 0.2	1.5	< 0.2	< 0.2	0.003	0.034
PD-1	6.25	1.01	< 0.2	1.2	< 0.2	< 0.2	0.002	0.027

Table A-2. Trace metal concentration data for surface sediment samples taken in Wilgreen Lake.

(Sample)	Mass (g)	Antimony	Arsenic	Cadmium	Chromium	Cobalt	Copper
		ppm	---				
blank 1		< 0.1	3	< 0.1	3	< 0.1	0.2
blank 2		< 0.1	4.1	< 0.1	< 0.5	< 0.1	0.2
gM2	0.5051	< 0.1	12.4	0.4	41.2	24.4	14.9
gTF-1	0.5064	0.1	20.6	0.5	63.4	39.5	12.5
gTF-1d	0.5056	< 0.1	6.1	0.4	16.9	10.6	16.9
gM3	0.5005	0.1	5.1	0.4	17.1	11.1	18
gTF-2	0.5012	< 0.1	3.8	0.4	17	10.9	16.7
gTF-2d	0.5080	0.1	5.8	0.5	21.3	12	19.5
gTF-3	0.5128	0.1	10.1	0.5	21	12.6	20.2
gTF-3	0.5065	< 0.1	3.6	0.3	19.7	12.2	18.6
gTF-4	0.5078	0.2	7.9	0.4	22.1	12.6	19.5
gTF-4d	0.5007	0.2	4.7	0.4	25.4	12.8	19.7
gTF-5	0.5187	0.1	7.7	0.5	23.5	13.1	20.6
gTF-5d	0.5028	0.1	8.6	0.4	21.9	12	18.7
gTF-6	0.5036	0.1	9	0.7	19.8	11.4	18.7
gM4	0.5068	< 0.1	5.8	0.3	14.3	10.9	12.1
gOTB-1u	0.5121	0.1	7	0.3	14.7	11	12.3
gOTB-1	0.5063	< 0.1	4.9	0.3	15.4	11.3	12.4
gOTB-1	0.5118	< 0.1	5.6	0.1	15.5	11.9	12
gOTB-1d	0.5107	0.1	6.8	0.4	16.5	11.6	14.2
gOTB-2	0.5065	< 0.1	6	0.4	21.8	12.7	15.9
gM5	0.5053	< 0.1	5	0.4	16.7	12.1	13.7
gPD-1u	0.5167	0.1	4.2	0.4	17.2	11.9	14.3
gPD-1	0.5145	< 0.1	7	0.4	22.3	13.1	17.8

Table A-2. Continued

(Sample)   Mass (g)

(Sample)	Mass (g)	Lead ppm	Nickel ----	Selenium	Silver	Thallium	Thorium
blank 1							
blank 2							
	0.5051	< 0.5	< 0.5	1	< 0.05	< 0.05	0.2
gM2	0.5064	0.5	< 0.5	1	< 0.05	< 0.05	0.2
gTF-1	0.5056	72.1	20.4	1.7	0.06	0.23	6.6
gTF-1d	0.5005	107	22.9	1.3	0.1	0.21	8.9
gM3	0.5012	33.6	15.8	1.1	0.09	0.19	5.6
gTF-2	0.5080	42.9	16.5	0.8	0.41	0.2	5.4
gTF-2d	0.5128	30.8	16.9	0.8	0.08	0.19	5.7
gTF-3	0.5065	31.3	20.6	1.2	0.08	0.22	6.7
gTF-3	0.5078	29.9	22.7	1.3	0.07	0.23	7.4
gTF-4	0.5007	30.2	22	1.7	0.06	0.19	7.1
gTF-4d	0.5187	29.8	24.3	1.1	0.08	0.23	7.5
gTF-5	0.5028	29.5	24.5	1.1	0.93	0.23	7.7
gTF-5d	0.5036	29.9	26.7	1.8	0.1	0.24	7.6
gTF-6		27.6	23.3	1.4	1.15	0.22	7.1
		25.5	22.5	1.6	0.16	0.22	6.5
gM4	0.5068	23.7	15.4	0.8	0.07	0.16	5.4
gOTB-1u	0.5121	24.6	15.4	0.9	0.09	0.17	5.7
gOTB-1	0.5063	22.7	15.4	0.5	0.06	0.18	5.5
gOTB-1	0.5118	23	14.9	1.3	< 0.05	0.15	5.2
gOTB-1d	0.5107	23.7	17.1	0.8	0.12	0.17	5.7
gOTB-2	0.5065	26.7	22.7	0.6	0.11	0.21	7
gM5	0.5053	26.5	17	0.5	0.23	0.18	5.8
gPD-1u	0.5167	23.9	18.8	1	0.14	0.15	6.3
gPD-1	0.5145	28.6	24.8	1.2	0.11	0.22	
7.6							

Figure A-1. *Water samples taken from stations in Taylor Fork, Old Town Brach, and Pond Creek, showing shallow and deep samples in oxic, disoxic, and anoxic zones. The dashed line representing KDW (Kentucky Department of Water) acute concentration threshold. Refer to (Fig. 2) for station locations.*
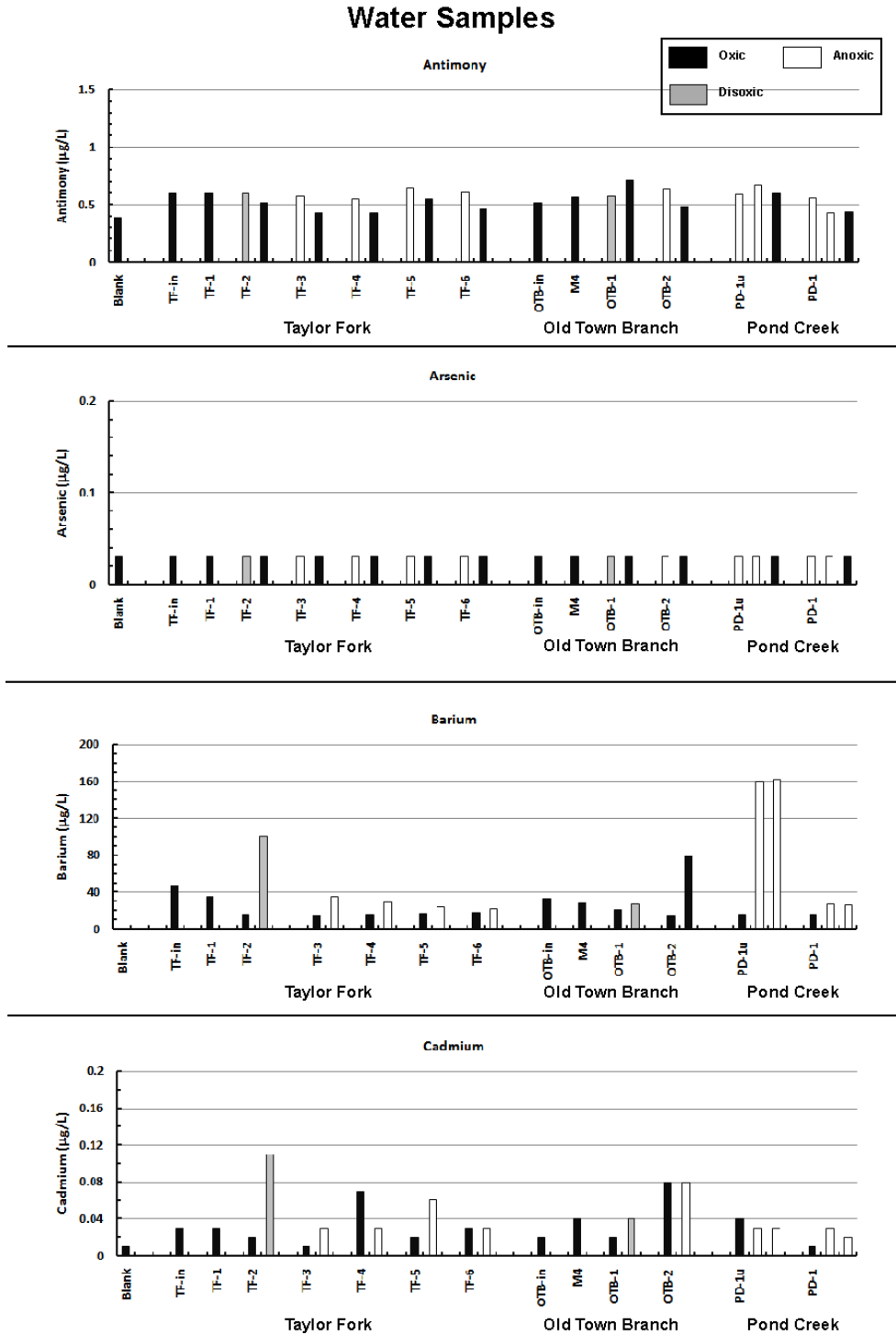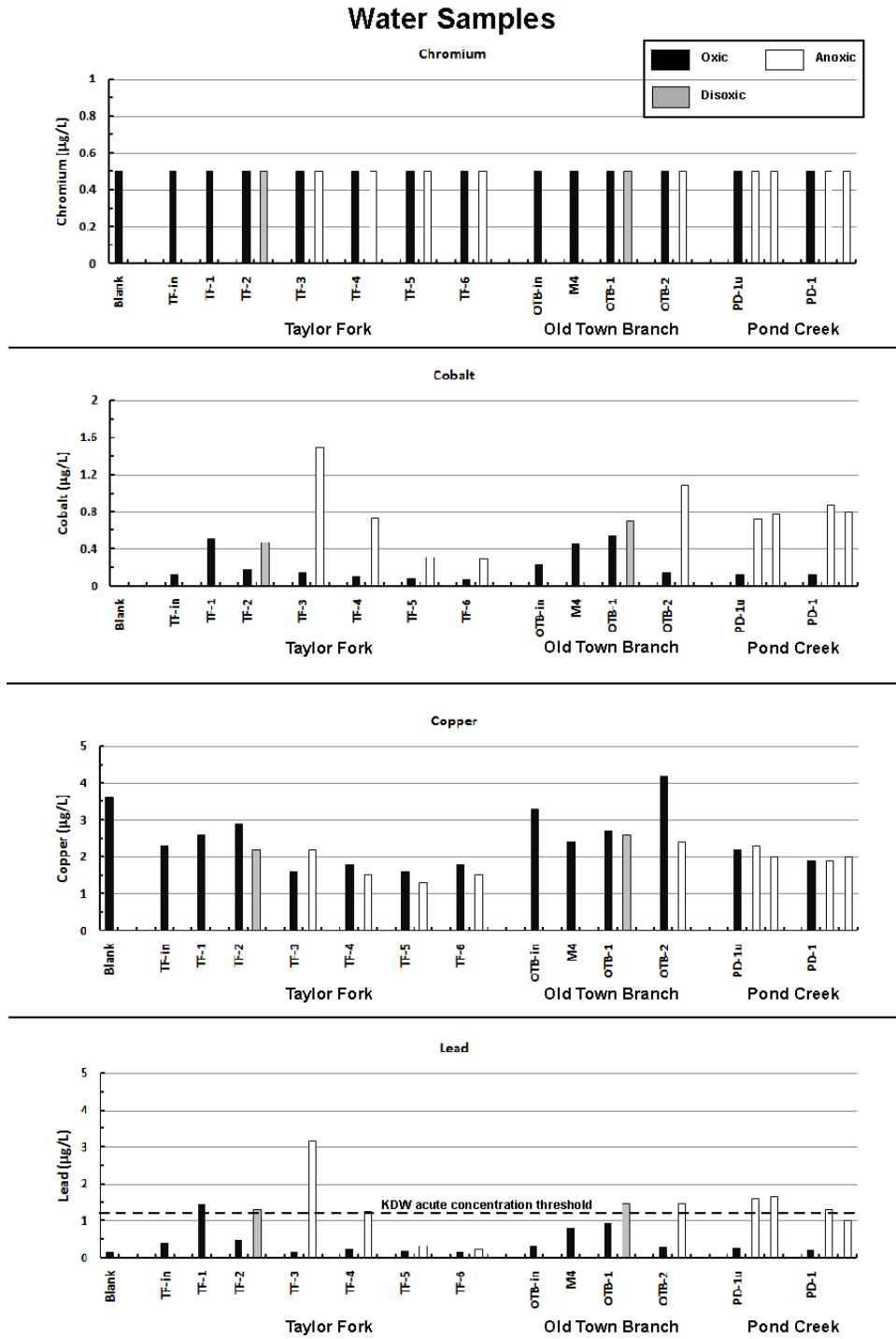
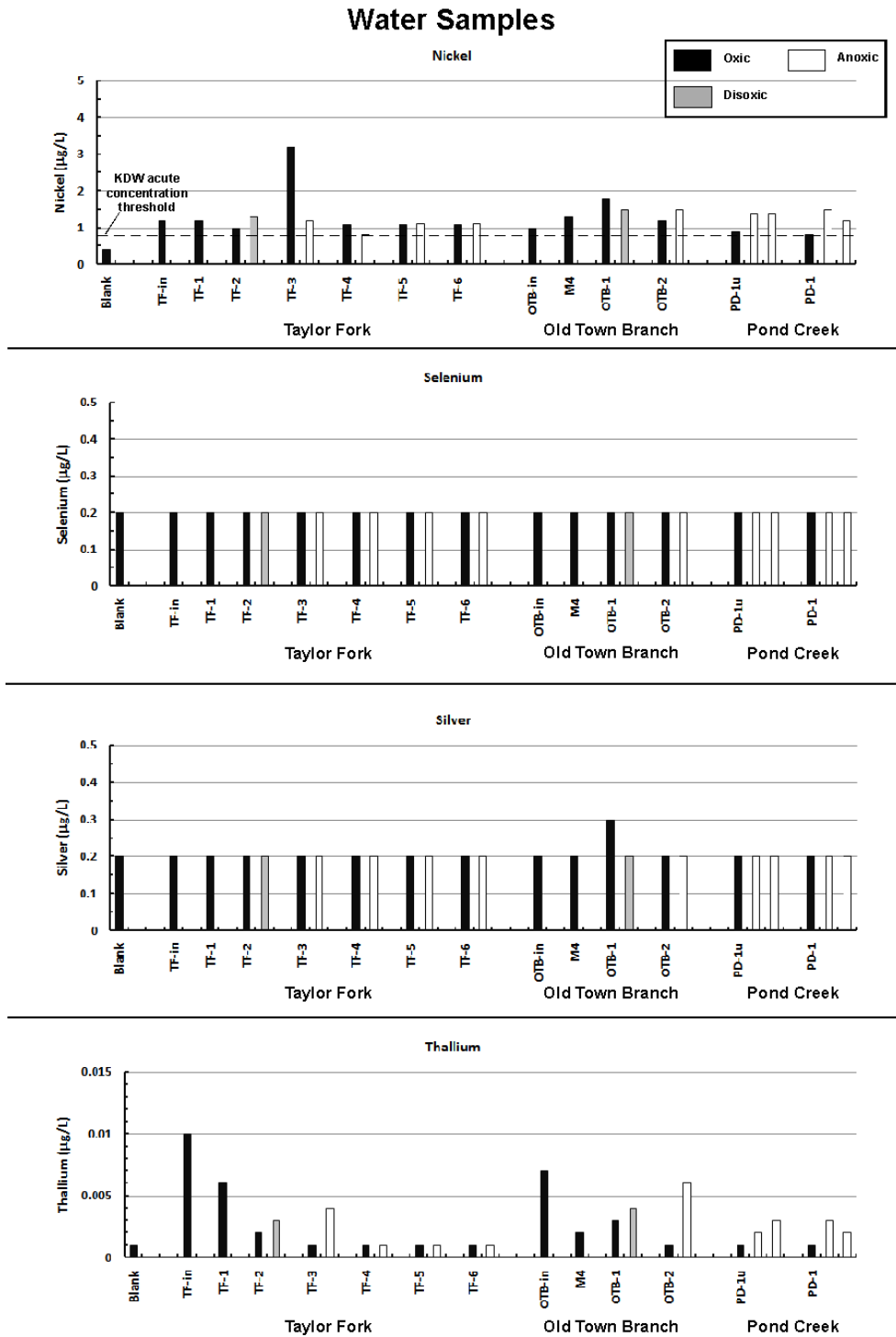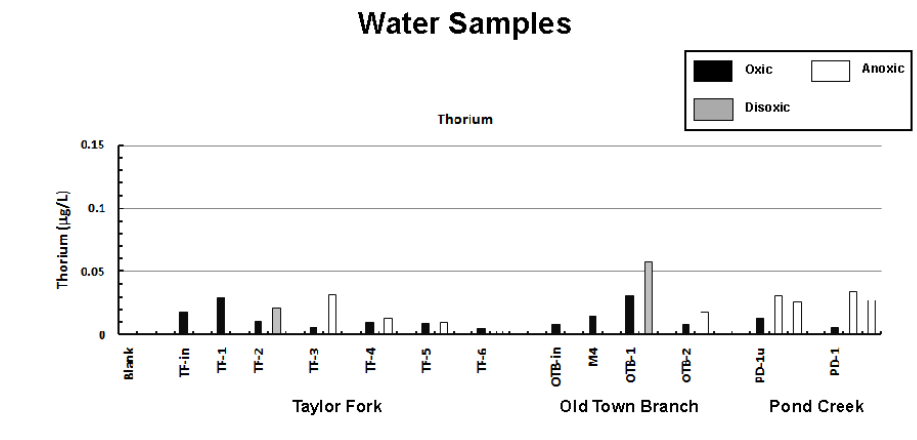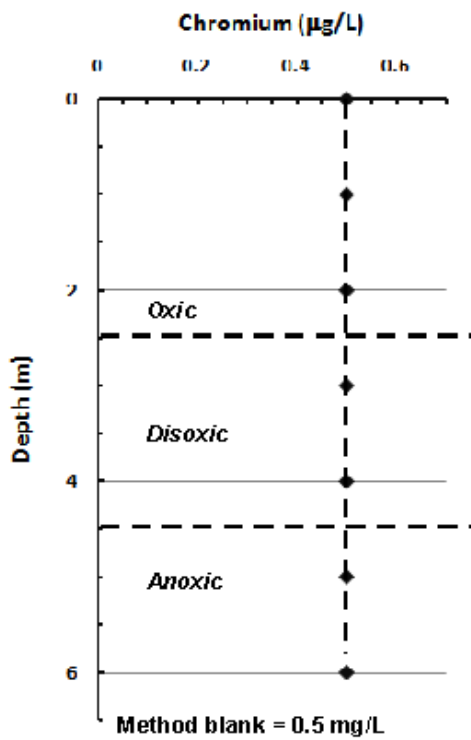*Figure A-1. Continued.*

Figure A-1. Continued.

Figure A-1. Continued.

Water Samples

***Figure* A-2.** *Water column profiles showing shallow and deep samples in oxic, disoxic and anoxic zones. Entire water-column profile collected at Station TF-3 (see Figure 4).*
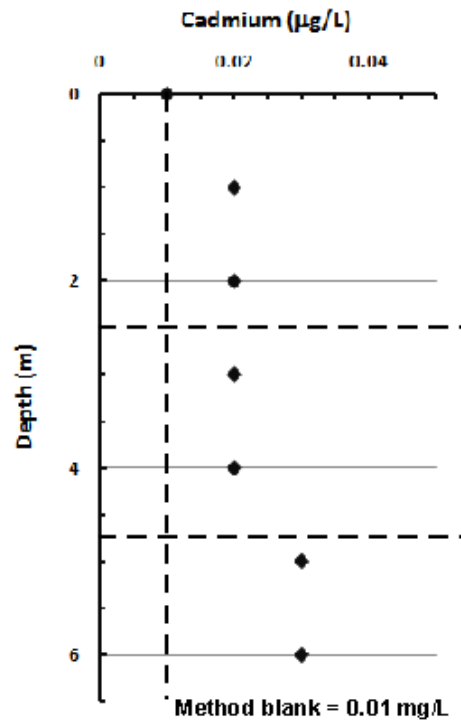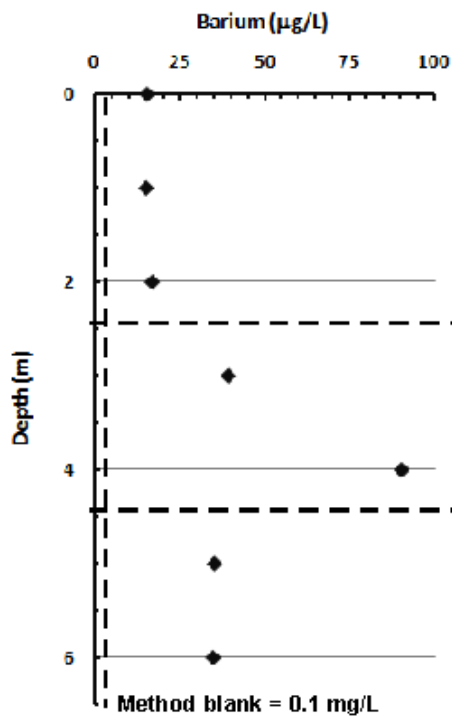
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Figure A-2. Continued.

Figure A-2. Continued.

Figure A-2. Continued.