Carcinogens within Lake Macatawa

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Intro:

Lake Macatawa has been a port of interest for both recreational and environmental activities. Back in the early 1900's Lake Macatawa was a major vacation resort for the white collar workforce of Chicago. At its peak, daily ferries would be moving people to and from the resorts, which have now burned down, to the heart of Chicago and back. It wasn't long after, industrial complexes started popping up along the lakes edge, producing everything from power, leather, pigments and even pickles. Along with the introduction of these new found companies came the introduction of the possible environmental issues in the Macatawa watershed. During this time of economic growth there were few to little regulations or protection towards the environment, resulting in the release of harmful chemicals into surrounding bodies of water, including Lake Macatawa.

In the mid 1900's, boaters where reporting the hauls of their boats were turning a bluish hue after a summer riding through the waters of Lake Macatawa. This caused some concern with the local population and concerns about the lake, leading to the local Government to step in. Eventually companies stopped dumping into Lake Macatawa directly and found some other means of disposing of their waste. Although the direct dumping into the lake stopped, the new fixes to Lake Macatawa's problems weren't the best solutions. In some cases, settling ponds where used to settle out the companies final effluent solids. Most of these ponds where not properly lined or properly taken care of, which led to the contaminants that were initially traveling directly into the lake now were traveling downward through the underlying sediments, causing another problem below the ground surface. Due to its longevity, sediment contamination can last longer in the environment than the contamination of just water because of its lack of ability to be mobile. The type of contamination can also play an important role in the overall longevity and toxicity of a certain area.

Industrial complexes around Lake Macatawa have diminished in the recent years but their footprints may still be apparent within the lake Macatawa's sediment. Contamination within the lakes sediment can be long term and the type of contamination that can play an important role in the overall longevity and toxicity of certain areas. Our area of interest for this study is a decommissioned pigment factory on Lake Mac's north shore where a spill occurred in the 1950's. This spill, as a one time event, dumped 3, 3'-Dichlorobenzidine which is used in the pigmentation process.

3, 3'-Dichlorobenzidine is not found naturally in the environment. It is an organic compound used for pigments for printing inks, textiles, plastics and enamels, paint, leather, and rubber. DCB itself is known to be a carcinogen within laboratory animals but has never been tested on humans. Benzidine on the other hand, 3, 3'-Dichlorobenzidines decay product, is a known carcinogen and causes cancer in the liver, bladder and tissues. These levels can still be found today within Lake Macatawa's sediment in a recent study done by Dr. Nyman et al 5 years ago.

Dr. Nyman et al found levels of 3, 3'-Dichlorobenzidine and its decay, Benzidine within Lake Macatawa sediment. From her study, we have posed additional questions and hypothesize to further investigate the extent of contamination from that spill in addition to updating her findings. For our testing hypothesis, we asked whether these organic compounds, DCB and Benzidine, had any effects on the immediate population, whether the concentration levels have decreased increased or disappeared entirely and whether the spill is moving or stationary.

Methods:

For this study, a prior study done by Nyman et al was used as the basis for the procedure. Sampling on the Lake Macatawa sediment was done from a pontoon boat at different points on the lake both in where the previous study was conducted as well as points upstream and downstream of the flow of Lake Macatawa. Figure 1 at the end of this report is a map of the sample sites used by our study as well as the sites used in the Nyman study. Samples were collected from the various points using a Ponar grab sampler. Once the samples were extracted from the lake bottom, they were placed into Ziploc bags and labeled with site number, GPS coordinates and date collected. Once all the samples were collected, they were placed in a refrigerator until they were needed for testing.

Analysis on the sediment samples was done using the High Performance Liquid Chromatography unit at Hope College. Using the samples gathered from the Ponar grab sampler, 4g of sediment was treated with 5mL of methanol and rotated over night. The sample was then centrifuged at 1350g for 20 minutes and the liquid on the top of the sample was filtered through a vacuum filtration system and then pipette into a HPLC vial to then be analyzed.

After the samples had been run, a standardized curve for DCB was calculated using a standard of DCB purchased from Sigma Aldrich. The standard curve can be found at the end of this report listed as Figure 2.

Results:

The results of our study were conclusive with Nyman's results. Figure 3 shows Nyman's table of results she collected during her study. Figure 4 shows one of the sites sampled by us that corresponds to Nyman's data and Figure 5 shows the suspected point source of the contamination. Overall, our data matches up with Nyman's data, indicating that the levels of DCB are in fact going down. Fig 6 shows this correlation between our sites and Nyman's sites.

Conclusions:

Some conclusions that we can come about this are that we did find some DCB on the sites that Nyman et al had previously. Along with the concentrations showing a lower count than what she had. We can see that the levels of DCB are in fact decreasing, but a big question that we need to find out would be is to where it is going and or even breaking down. We have not tested for levels of benzidine, which is the decay product of DCB. Benzidine levels could be increasing or possibly flowing through the groundwater, but that is undeterminable and can be used for future research. We can conclude that the levels of DCB are decreasing and that the levels were not toxic 5 years ago and since then the levels are even lower. There is no threat to the toxicity levels in the lake but future testing could be applied about 5 years later to proceed with an update on the levels as well as measure the levels of benzidine and the toxicity of it. Possible future research on these sites would be by going into each site and grabbing a core using some form of piston corer to try and determine depth and horizontal sediment profiles to possibly find out what layer the DCB or benzidine might traveling at.

References

Nyman, Marianne C., Arto K. Nyman, Linda S. Lee, Loring F. Nies, and Ernest R. Blatchley. "3,3' –Dichlorobenzidine Transformation Processes in Natural Sediment." *Environmental Science Technology* 31 (1997): 1068-73. Print.

http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=703&tid=126

http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=958&tid=200

http://www.epa.gov/iris/subst/0447.htm

Acknowledgments

We would like to give a big thanks to Dr. Brian Bodenbender[1], Dr. Kenneth Brown[2], Dr. Jason Gillmore[2], Dr. Graham Peaslee[2], and Dr. Michael Seymour[2], as well as our former employee of the industrial pigment factory for all their help and support through the process of this research project.

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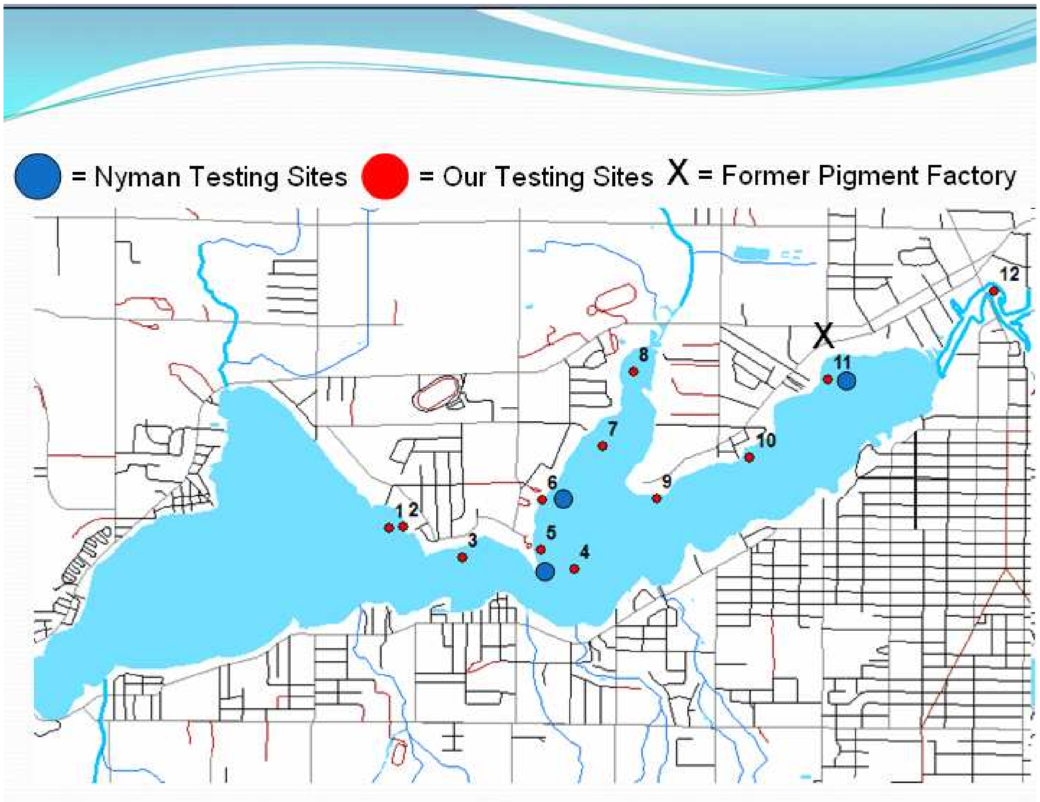
[2]Hope College Chemistry Department, Holland, Michigan

Fig 1:


= Nyman Testing Sites
= Our Testing Sites
X = Former Pigment Factory
1
2
3
4
5
6
7
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9
10
11
12
X

Fig 2:

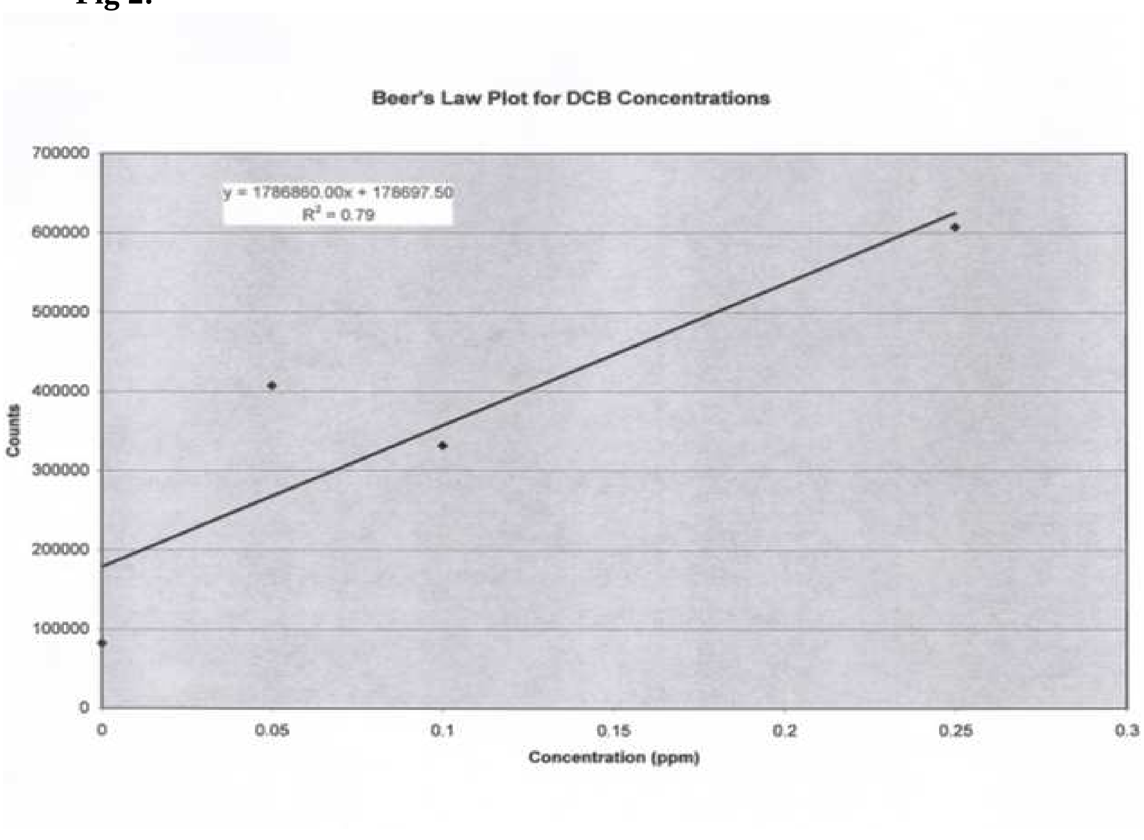

Beer's Law Plot for DCB Concentrations
y = 1786860.00x + 178697.50
R² = 0.79
Counts
Concentration (ppm)
0
100000
200000
300000
400000
500000
600000
700000
0
0.05
0.1
0.15
0.2
0.25
0.3

Fig 3:

Table 3
Chlorobenzidine burdens in the sediment phase during the over 11-year study

ID	DCB (mg/kg)	Benzidine (mg/kg)
1993		
I-93	ND	YES
II-93	ND	YES
III-93	0.066	ND
V-93	69.663	ND
VII-93	0.085	YES
VIII-93	0.038	ND
X-93	3.05	ND
1994		
I-94	0.049	1.503
II-94	0.037	62.662
III-94	0.279	ND
1996		
I-96	0.013	1.28E–4
II-96	0.030	2.17E–4
III-96	0.031	3.37E–4
IV-96	0.027	0.069
V-96	0.017	03.93E–4
VI-96	0.008	1.24E–4
VII-96	0.011	7.26E–4
VIII-96	0.041	6.27E–4
IX-96	0.031	2.54E–4
X-96	0.012	3.70E–4
XI-96	0.012	2.10E–4
XII-96	0.052	3.73E–4

Fig 4:

D-7500 INTEGRATOR REPORT

ANALYZED: 11/13/10 00:04 REPORTED: 11/13/10 00:20
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>

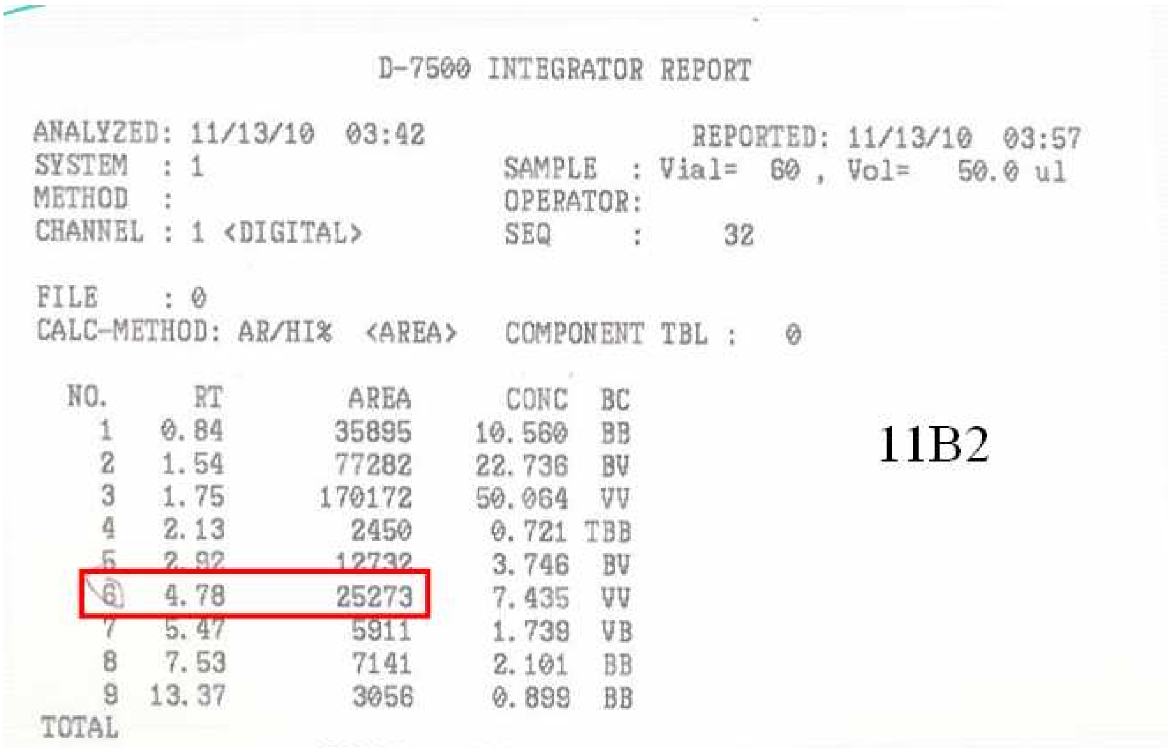
SAMPLE : Vial= 47 , Vol= 50.0 ul
OPERATOR:
SEQ : 19

FILE : 0
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	0.83	65821	8.570	BB
2	1.36	5475	0.713	BV
3	1.54	83217	10.835	VV
4	1.74	566608	73.773	VV
5	2.13	1519	0.198	TBB
6	2.51	1102	0.143	TBV
7	3.36	9557	1.244	TVV
8	4.65	25220	3.284	TVB
9	6.22	718	0.093	TBB
10	7.58	5755	0.749	BB

6A

Fig 5:



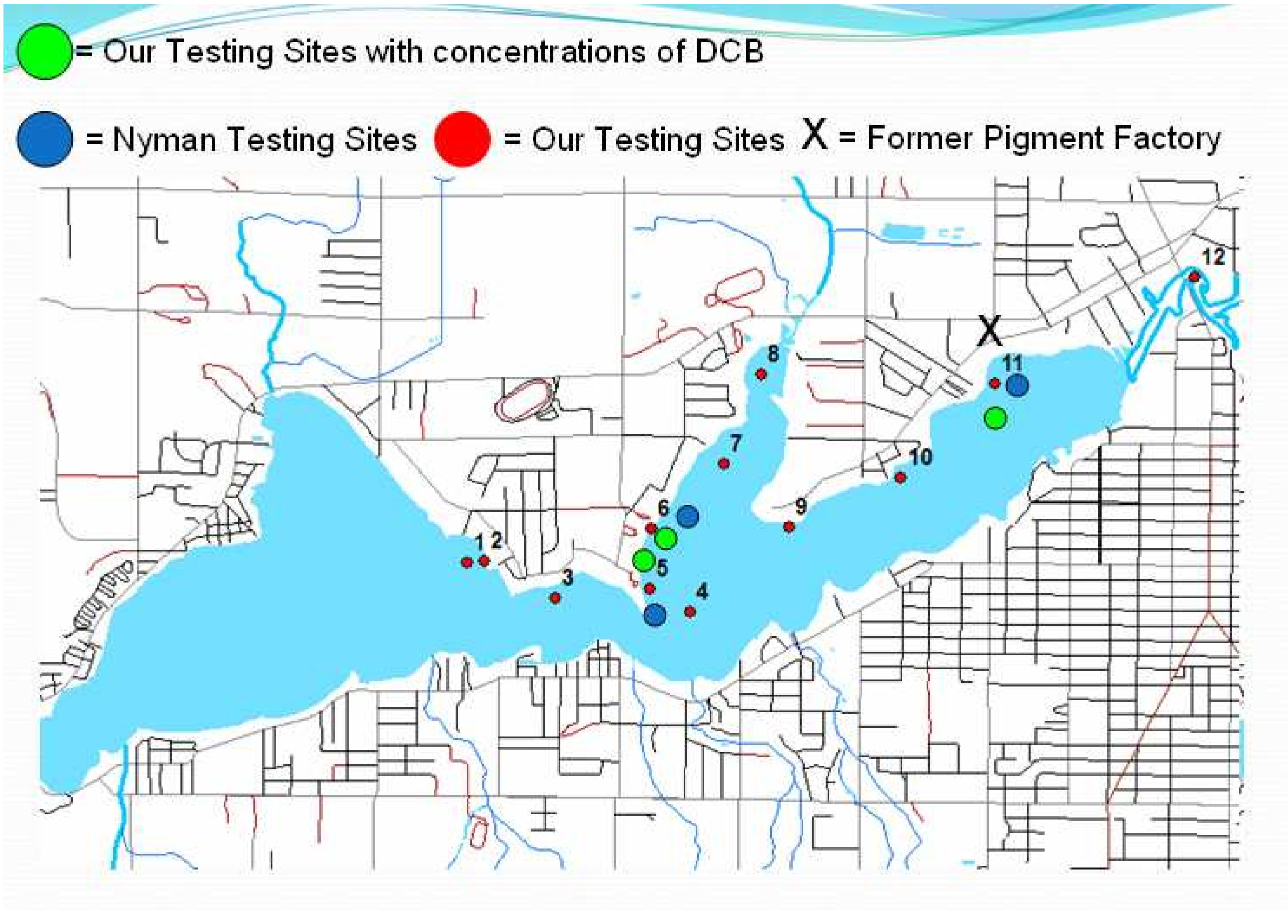
D-7500 INTEGRATOR REPORT

ANALYZED: 11/13/10 03:42 REPORTED: 11/13/10 03:57
SYSTEM : 1 SAMPLE : Vial= 60 , Vol= 50.0 ul
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 32

FILE : 0
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	0.84	35895	10.560	BB
2	1.54	77282	22.736	BV
3	1.75	170172	50.064	VV
4	2.13	2450	0.721	TBB
5	2.92	12732	3.746	BV
6	4.78	25273	7.435	VV
7	5.47	5911	1.739	VB
8	7.53	7141	2.101	BB
9	13.37	3056	0.899	BB
TOTAL				

Fig 6:



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