

NEUTRON ACTIVATION ANALYSIS OF SAMPLES TAKEN FROM THE
LAKE MILTON BED AND VARIOUS SURROUNDING TRIBUTARIES

by

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Submitted in Partial Fulfillment of the Requirements
for the Degree of
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ABSTRACT**NEUTRON ACTIVATION ANALYSIS OF SAMPLES TAKEN FROM THE
LAKE MILTON BED AND VARIOUS SURROUNDING TRIBUTARIES****KRISTINE HEIPEL****MASTER OF SCIENCE IN CHEMISTRY****YOUNGSTOWN STATE UNIVERSITY, 1988**

Lake Milton, through which the Mahoning River flows, was a recreational facility for many years, until the lake was drained in 1986. After the lake was drained, soil samples were cored from 31 locations along the dry lake bed and from surrounding tributaries.

The samples were oven dried, crushed and weighed, and then analyzed by neutron activation analysis (NAA), a sensitive analytical method for determining trace elements, at the Ohio State University Nuclear Reactor Laboratory (OSU-NRL) in Columbus, Ohio. From preliminary results, nine of the 31 sites were chosen for further analysis. The choice of sites was based on the concentrations of the following elements, which may be pollutants: As, Al, V, Ti, Co, Cr, Zn, and Ni. For the nine selected sites, the cored samples were divided into three portions, top, middle, and bottom. Thirty two elements (Mn, V, Ti, Na, Sc, Cr, Co, Rb, Ba, La, Sm, Yb, Lu, Th, Nd, U, As, Zn, Cs, Sb, Ca, Fe, Al, Eu, Tb, Se, Sr, Zr, Hf, Ta, Ce, and Ni) were determined by NAA for each of the 27 samples (nine sites, three portions per site).

Attempts were made to relate the results to the history and geography of the lake. Many sites located near inhabited areas and sites near or on the banks of the Mahoning River, contained elevated concentrations of various elements.

Eight elements (Ti, Fe, As, Ba, Co, Cr, Cs, and V) were found in elevated concentrations in samples taken from the lake bed. Four samples taken from the Canyon Park area contained elevated concentrations of these elements. However, due to the limited sampling of such a large area as Lake Milton, no definite conclusions can be drawn from the data concerning possible pollution or contamination.

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CHAPTER I

INTRODUCTION

Lake Milton is a man-made lake originally created in 1917 as a water supply for the city of Youngstown, Ohio, during the hot summer months.¹

When it was decided in 1906 that there was a need for a storage basin, a site was chosen in Berlin township, but before all the land could be obtained, private interests bought up the remaining land and blocked the sale of it unless the city of Youngstown bought it at much higher prices. It then became necessary to look for another location. The second choice was in Milton township, which was just north of the Berlin site.¹

The land needed for the Milton site was purchased by the city between 1912 and 1917, but it was not until the spring of 1917 that the dam was completed and the basin filled.²

Lake Milton served as a storage basin for drinking water until 1925, when the Ohio Department of Health condemned the Mahoning River (including the lake) as a source of drinking water because of sewage and industrial wastes found in the river.³ After 1925, the lake was used to supply industries with water, and during this time filtration plants were created for sanitation purposes.

Following the construction of the Meander Reservoir, which became Youngstown's source of drinking water, and after the construction of Berlin and Mosquito Reservoirs during World War II, Lake Milton became a recreational facility.

The lake, which is located 16 miles west of Youngstown, extends approximately seven miles in length, has 1685 acres of surface water, and can impound a maximum of 10 billion gallons of water. The lake is surrounded by 1171 acres of additional land purchased by the city.^{4, 5}

The lake was drained in February 1986 so that the dam could be repaired.⁵ When the dam was originally constructed, it was intended to restrain 2 billion gallons of water at normal summer levels, but it actually restrains 8-11 billion gallons.⁶ As a result, after 70 years, the dam needed much repair. The state funded the repair of the dam, and since the city of Youngstown could no longer afford the upkeep of the lake, the state took over the lake and made it into Ohio's 72nd state park.⁷ Refilling of the lake was scheduled to begin in the spring of 1988.

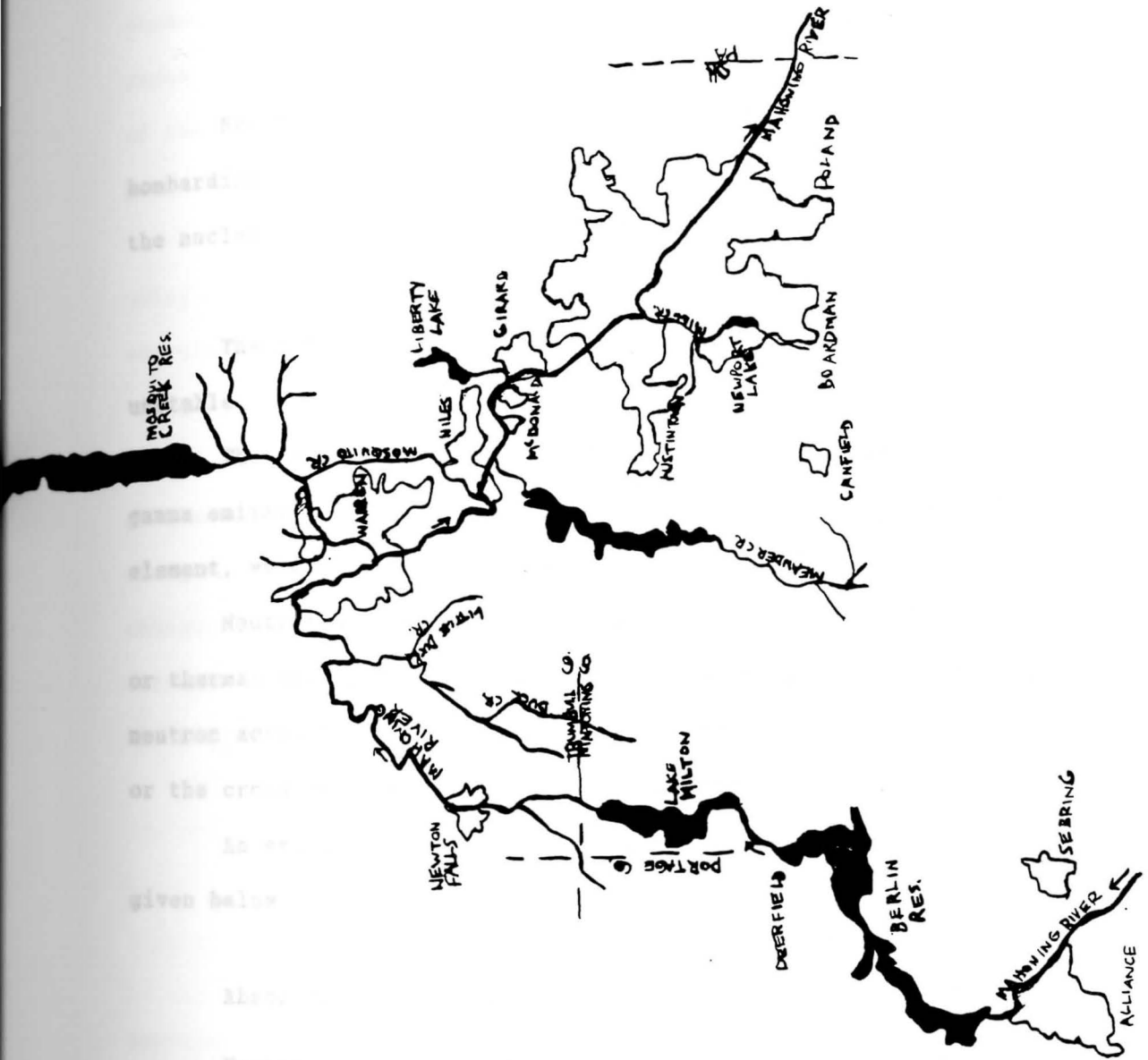
Previous studies at Y.S.U. have been conducted on the Mahoning River from Newton Falls to the Pennsylvania state line.^{8, 9} White found elevated concentrations of various elements in sediment samples of the river taken from an area directly north of Lake Milton.⁸ The area under investigation in this study is the drained Lake Milton bed, which is south of the previous investigations (see Figure 1). In this study we chose to investigate the trace element distribution as a function of site location along the lake bed and its surrounding tributaries, and as a function of depth at selected sites based on preliminary results.

The collected sediment samples were analyzed by neutron activation analysis (NAA) at the Ohio State University Nuclear Reactor Laboratory (OSU-NRL) in Columbus, Ohio. NAA was chosen as the method of analysis since no sample digestion is required and a large number

of elements can be analyzed. NAA also has the advantage of low detection limits.

The preliminary investigation involved the analysis of the surface sediments taken from 31 sites along the river channel, from the lake bed and from various surrounding tributaries feeding the lake. After analysis of the preliminary results, nine sites were selected for further depth analysis.

FIGURE 1

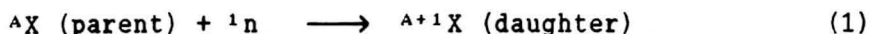


MAP SHOWING THE MAHONING RIVER

CHAPTER II

THEORY OF NEUTRON ACTIVATION ANALYSIS

Neutron activation involves irradiating an unknown material by bombarding it with neutrons, which are then captured (or absorbed) by the nuclei in the sample, as seen in equation 1.

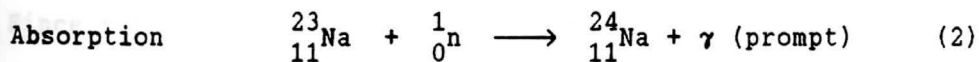


The resulting daughter nuclei are neutron rich and are usually unstable.

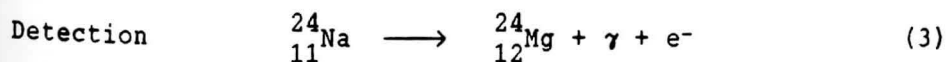
The daughter nucleus then decays by a beta process (followed by gamma emission) at a rate related to its half-life forming a stable element, which is one value higher in atomic number than the parent.

Neutron activation can be induced by fast (i.e., high energy) or thermal (i.e., slower or low energy) neutrons. Usually thermal neutron activation is used since the probability of neutron capture, or the cross section, is higher than for higher energy neutrons.

An example of a typical thermal neutron activation reaction is given below



Neutrons from a reactor are passed through a moderator (usually water) which slows them to thermal energies. A sample is placed in the source where the nuclei (${}^{23}\text{Na}$) absorb neutrons releasing ${}^{24}\text{Na}$ and a prompt gamma photon. The isotope produced (${}^{24}\text{Na}$) is neutron rich and hence unstable. It then decays as shown below



^{24}Na decays to give ^{24}Mg , which is stable, and another gamma photon is emitted. The gamma photons emitted here (not the prompt gamma photon mentioned earlier) have energies which are characteristic of the individual nucleus. No two different isotopes have the same gamma photon energies.

The gamma radiation energy from the beta decay can be measured using gamma spectroscopy. Both the characteristic gamma photon energies and the half-life of the unstable nucleus (^{24}Na) are a "fingerprint", thus identifying the element present, ^{24}Na .

Neutron activation is done on a comparative basis rather than an absolute basis. The standard of known concentration is irradiated along with the unknown sample. By doing this, any errors due to changes in the neutron flux with time are eliminated. If the same detector and geometry are used to measure both standards and unknowns, the following two equations can be derived.

$$A_{\text{unknown}} = N_{\text{unknown}} \times \text{constant} \quad (4)$$

$$A_{\text{standard}} = N_{\text{standard}} \times \text{constant} \quad (5)$$

Where A = activity measured by the detector
N = number of target nuclei

Since the geometry, flux, and cross section are the same, and assuming the same isotopic abundances, these two equations can be rewritten as

$$\frac{A_{\text{unknown}}}{A_{\text{standard}}} = \frac{N_{\text{unknown}}}{N_{\text{standard}}} \quad (6)$$

N_{standard} is known, and both activities are measured. Equation 6 can then be rearranged and solved for N_{unknown}

$$N_{\text{unknown}} = \frac{A_{\text{unknown}}}{A_{\text{standard}}} \times N_{\text{standard}} \quad (7)$$

The following equation is the general equation for measuring the activity of the radiation produced by thermal bombardment.¹⁰

$$A = N \phi \epsilon \sigma m G \left[1 - e^{\left(\frac{-0.693 \times t}{t_{1/2}} \right)} \right] \quad (8)$$

where ϕ = neutron flux in n/cm² s (* see below)
 σ = reaction cross section in cm²
 ϵ = detector efficiency
 m = isotopic abundance of nuclei
 G = geometric factor of detector
 t = irradiation time
 $t_{1/2}$ = half-life of nucleus

* The higher the neutron flux, the greater the number of target nuclei activated, which results in greater sensitivity of detection.

Assuming the same isotopic abundances, geometry, cross section, flux, etc., equation 8 reduces to equations 4 and 5.

Neutron activation analysis is a sensitive method and is also non-destructive, unlike atomic absorption (AA) and inductively coupled plasma (ICP), which require sample digestion and/or chemical separation. NAA is non-destructive in the sense that the samples can be reused for other methods as the change in composition is negligible. A disadvantage of neutron activation is that information about the oxidation or chemical states is not determinable.¹¹

CHAPTER III

EXPERIMENTAL PROCEDURES

SAMPLE COLLECTION

Samples were collected from October 31 through November 14, 1987, from 31 locations along the river channel, surrounding tributaries, and from various locations in the drained lake bed. A list of sample sites and collection dates is given in Table 1. See Figure 2 for site location.

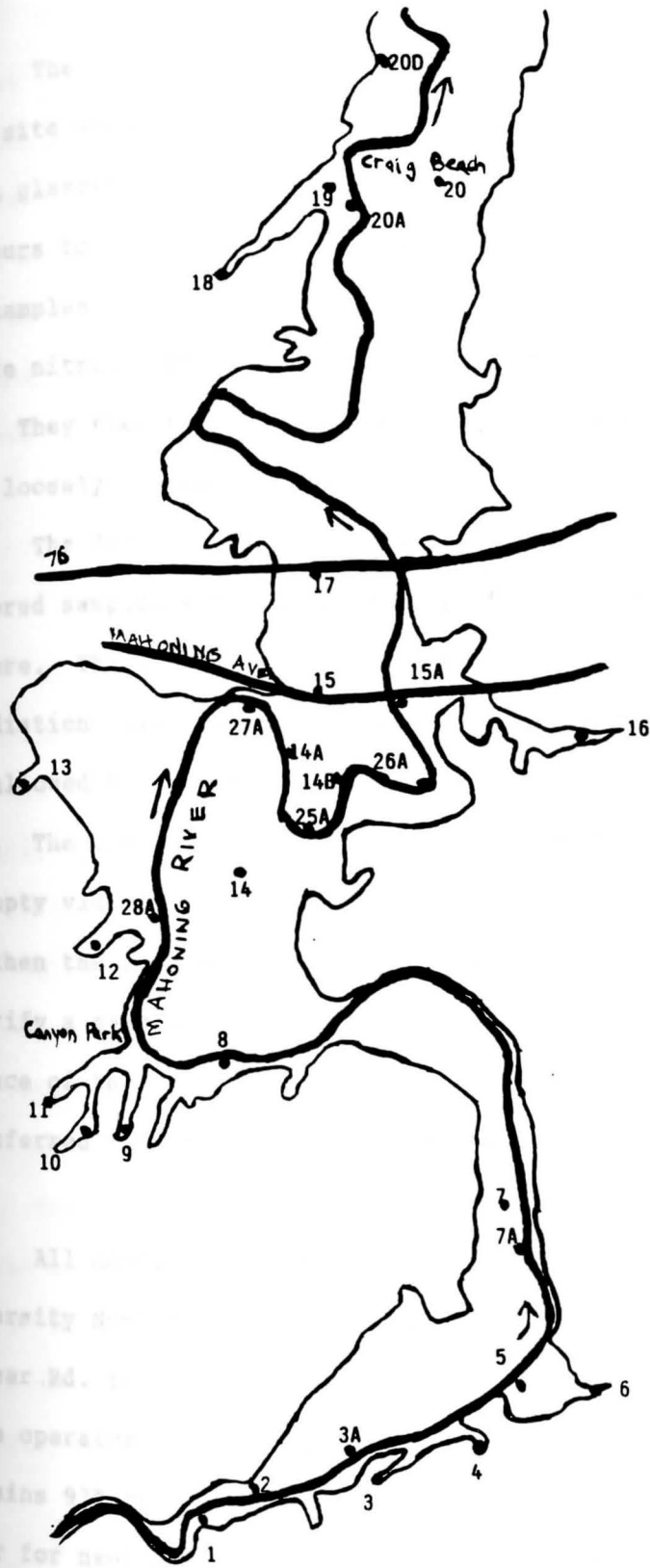
Samples were taken at each site using a metal tube one foot in length and one inch in diameter with a handle that extended an additional two feet, called a sample corer. After a sample was cored, it was transferred onto plastic wrap, and then wrapped and labeled for later use. The cored samples were 12 inches in length and marked into top, middle (0.5 inch long sample taken 5.5-6 inches from the top), and bottom (0.5 inch long sample taken 11-11.5 inches from the top) portions. In transferring the cored samples onto plastic wrap, the very top portion, (about 1 inch in length), often did not come out of the corer. To avoid this problem, a different method was used to obtain a top sample. A plastic scoop was used to scrap away the top soil and then a sample was removed. These top portions (all 1 inch in depth) were transferred into precleaned polyethylene vials and labeled.

Cored samples were obtained for all sites except site 16. For this particular site, only a top sample was obtained because the sample corer would not go down further than 6 inches (halfway) due to rock formations.

TABLE 1
List of Sample Sites and Collection Dates

<u>Site</u> (in order of collection)	<u>Date Collected (1987)</u>
15A	October 31
15	October 31
14B	October 31
25A	October 31
14A	October 31
17	October 31
2	November 1
1	November 1
3A	November 1
5	November 1
4	November 1
18	November 8
19	November 8
20D	November 8
20	November 8
20A	November 8
10	November 11
11	November 11
9	November 11
8	November 11
6	November 11
3	November 11
7A	November 11
7	November 11
26A	November 14
27A	November 14
16	November 14
14	November 14
12	November 14
28A	November 14
13	November 14

FIGURE 2



MAP OF LAKE MILTON SHOWING SITE LOCATIONS

SAMPLE PREPARATION

The top, middle, and bottom portions of the cored samples for each site were placed in individual mortar dishes and covered with watch glasses. They were then placed in an oven set at 100-110°C for 24 hours to dry the samples. The mortar and pestles, the vials for the top samples, and the watch glasses were precleaned by soaking them in dilute nitric acid (doubled distilled, approx. 5%) for three to four days. They then were rinsed with deionized water and allowed to air dry, loosely covered to protect them from dust and foreign debris.

The dried samples were then crushed to a fine powder. The powdered samples were thoroughly mixed to ensure a homogeneous mixture. The samples were then transferred to polyethylene irradiation vials which were precleaned by soaking in absolute alcohol and allowed to air dry, also loosely covered to protect them from dust. The cleaned vials were then handled with gloves. After taring an empty vial to zero, 100-200mg of a sample was placed in the vial, and then the sample weight was read directly from the balance. To identify a sample in a vial, a numerical code was scratched on the surface of the vial. The remainder of the powdered samples were transferred into individual labeled sealed plastic bags for later use.

OSU-NRL

All neutron activation analysis work was done at the Ohio State University Nuclear Reactor Laboratory (OSU-NRL), which is located on Kinnear Rd. in Columbus, Ohio. The reactor is a pool type reactor which operates at a maximum power level of 10 kW. The reactor core contains 93% enriched uranium-235 fuel, and is surrounded by light water for neutron moderation, radiation shielding and for cooling.

The irradiated samples were measured using gamma spectroscopy at the OSU-NRL. The detector used was a Princeton lithium drifted germanium [Ge(Li)] detector. The entire detector was shielded to reduce background radiation. The detector was connected to a Canberra multi channel analyzer (MCA), which had a 4096 channel memory. The MCA was interfaced to a computer which had a hard disk for storage of spectra, and also contained a comparison analysis program. The program calculated concentrations of elements according to equation 7.

PROCEDURE

INITIAL STUDY

All top samples for the 31 sites were irradiated with five standards, which were provided by the OSU-NRL. Of the five standards, two were the International Atomic Energy Agency (IAEA) reference material, IAEA soil-5. The third standard was also an IAEA reference, IAEA soil-1. The fourth standard was a National Bureau of Standards (NBS) reference, NBS 1645. Finally, the fifth standard was an IAEA reference, IAEA soil-7. The two IAEA soil-5 standards were used in the computer comparison. The three remaining standards were analyzed as unknowns as an instrument backup check.

The 31 top samples and the five standards were first analyzed for the shorter-lived isotopes Al-28, V-52, Ti-51, and Mn-56. The samples were irradiated one at a time for five minutes using the rabbit facility (a pipe system which allows a sample to be sent into and taken out of the reactor core by means of compressed air). The

samples were measured within 2-3 minutes after irradiation. The neutron flux in the rabbit system was 4×10^{10} n/cm² s.

The 31 top samples and the five standards were then irradiated for 7.5 hours in the center of the core. Measurements were made after a 7 day decay period (where the longer-lived isotopes are the most active and are detected) and after a 40 day decay period (for detection of the longest-lived isotopes that were previously undetected due to masking by the more active isotopes from the 7 day decay, which after 40 days, are less active), see Tables 2 and 3. The neutron flux at the center of the core was 2×10^{11} n/cm² s.

When an element appeared in both the 7 day and the 40 day counts, the concentration of the element from the 7 day counts was used rather than the results from the 40 day counts. The reason is that the concentration of the 7 day counts more closely reflected the initial concentration of the elements present.

FURTHER STUDY

After careful analysis of the results obtained for the top samples of the 31 sites, it was decided that further analysis would be done on the middle and bottom samples of various selected sites.

Based on elements that are associated with steel manufacturing as well as other pollutants that were determined in earlier studies, seven of the 31 sites were chosen for further analysis.¹² In addition to the seven chosen sites, two other sites were chosen for comparison purposes.

The following elements were of interest in choosing the sites for additional analysis: As, V, Ti, Cr, Co, Ni, Fe, and Zn. The

TABLE 2
Element and the Decay Period Necessary for Detection

<u>Element</u> (and isotope)	<u>Decay Period</u> (days)	<u>t$\frac{1}{2}$ of isotope</u>
Mn-56	0	2.579 hr.
Al-28	0	2.24 min.
Ti-51	0	5.80 min.
V-52	0	3.76 min.
Na-24	7	15.02 hr.
Sc-46	7*	83.80 day
Cr-51	7*	27.70 day
Co-60	7*	5.271 yr
Rb-86	7*	18.8 day
Ba-131	7*	12.0 day
La-140	7	40.3 hr.
Sm-153	7	46.8 hr.
Yb-175	7**	4.19 day
Lu-177	7	6.71 day
Th-232	7*	1.41 x 10 ⁶ yr
Nd-147	7*	11.0 day
U-238	7*	4.468 x 10 ⁹ yr
As-76	7*	26.3 hr.
Zn-65	7*	244.1 day
Cs-134	7*	2.062 yr
Sb-122	7**	2.68 day
Ca-47	7	4.536 day
Fe-59	7*	44.6 day

* Measured in both seven (7) day and forty (40) day counts.

**Different isotopes of the same element:

Yb-175	7 day	Sb-122	7 day
Yb-169	40 day	Sb-124	40 day

TABLE 3
Element and the Decay Period Necessary for Detection

<u>Element</u> (and isotope)	<u>Decay Period</u> (days)	<u>t_{1/2} of isotope</u>
Eu-152	40	13.0 yr
Tb-160	40	72.1 day
Yb-169	40**	32.0 day
Sc-46	40*	83.80 day
Cr-51	40*	27.70 day
Fe-59	40*	44.6 day
Co-60	40*	5.271 yr
Se-75	40	118.5 day
Sr-85	40	64.8 day
Zr-95	40	64.0 day
Sb-124	40**	60.20 day
Ba-131	40*	12.0 day
Hf-181	40	42.4 day
Ta-182	40	115.0 day
Ce-141	40	32.5 day
Zn-65	40*	244.1 day
Nd-147	40*	11.0 day
Rb-86	40*	18.8 day
Ni-59	40	8.0 x 10 ⁴ yr
Th-232	40*	1.41 x 10 ¹⁰ yr
Cs-134	40*	2.062 yr
U-238	40*	4.468 x 10 ⁹ yr

* Measured in both seven (7) day and forty (40) day counts.

**Different isotopes of the same element:

Yb-175	7 day	Sb-122	7 day
Yb-169	40 day	Sb-124	40 day

seven sites chosen for the analysis of the middle and bottom samples were sites 6, 10, 11, 7A, 20A, 26A, and 28A. The two additional sites chosen for comparison to the original seven were sites 4 and 14.

As can be seen from Figure 2, six of the seven chosen sites are located in the southern part of the lake. The seventh site (site 20A), is the only site that is located in the northern part of the lake (sites ending in the letters A or B denote river channel sites).

Since the Mahoning river flows from the Berlin Reservoir (which is south) north through the Craig Beach area, it would be expected that whatever suspended pollutants and/or minerals that the river was carrying would be deposited when the river enters into a larger slower moving body of water. Any dissolved particles would be carried by the river further downstream and would be uniformly distributed throughout the area.

Some possible reasons that site 20A contains relatively high concentrations of various elements is that it is near a filtration plant and is also located in a relatively populated area.

The two sites that were chosen in addition to the seven others were chosen because of their location. Site 4 was chosen because it was in the southern part of the lake and other sites around it contained elements in relatively high concentrations. Site 14 was chosen because of its location in the lake bed.

The middle and bottom samples of the nine sites were prepared as were the top samples. Again the remainder of the samples were kept for later use by storing them in individual sealed and labeled plastic bags.

The procedure for the analysis of the middle and bottom samples was identical to that used for the top samples. The short-lived isotopes were analyzed first, followed by irradiating the samples and standards for 7 hours in the center of the core of the reactor. After irradiation, the samples were allowed to decay for a period of 7 days and then the concentrations were measured. The 40 day counts could not be done on these samples as was done with the top samples, the reason being the OSU-NRL facility temporarily closed down on June 1, 1988 to refuel.

Data from Tables 5-9 and 5-10 are presented for the 31 samples. The concentration of the isotopes was also chosen to be the concentration of the 31 samples for the

For all of the isotopes the concentrations were determined and the reported concentration error from the differences between the reference counting station and these values is 15%. Tables 5-9 and 5-10 are standard, IAEA

CHAPTER IV

RESULTS

Table 4 shows the average concentration in parts per million (ppm or $\mu\text{g/g}$) of various elements found naturally in the earth's crust.¹³ This table is intended to provide a general indication of the amounts of various elements that are available in rocks and minerals for possible solution by water, which will eventually form lake or river sediments.

Data from NAA of the samples are listed in Tables 5-34, where Tables 5-9 show the initial data obtained from the 0 and 7 day counts for the 31 top samples, Tables 10-32 are arranged by element and list the concentrations for the top, middle, and bottom portions of the nine chosen sites, and the remaining tables, Tables 33 and 34, list the concentrations of the elements from the 40 day counts of the top samples for the nine chosen sites.

For elements with multiple gamma peaks, concentration values were determined for each peak and the average of the values is the reported concentration. Each reported concentration value has an error from gamma counting statistics, plus an additional error due to differences between the measured and reported concentration values for the reference standard, IAEA soil-5. The errors from the gamma counting statistics for each element are averaged from all sites, these values are listed for top, middle, and bottom samples in Table 35. Tables 36 and 37 show the results of the analysis of the standard, IAEA soil-5, and the percent error.

TABLE 4

Average Composition of Elements Found in the Earth's Crust (in ppm)

ELEMENT	IGNEOUS ROCKS	SANDSTONE	SHALE	CARBONATES
Si	285000	359000	260000	34
Al	79500	32100	80100	8970
Fe	42200	18600	38800	8190
Ca	36200	22400	22500	272000
Na	28100	3870	4850	393
Mg	4830	1950	4440	377
Ti	937	392	575	842
Mn	595	193	250	30
Ba	368	28	290	617
Sr	198	120	423	7.1
Cr	166	197	243	46
Rb	160	204	142	18
Zr	149	20	101	13
V	130	55	45	11
Ce	94	2.6	29	13
Ni	80	16	130	16
Zn	56	24	18	8.0
Md	48	19	28	9.4
La	23	0.33	8.1	0.12
Co	16	6.6	5.0	1.1
Sm	15	0.73	10	0.68
Sc	11	3.9	13	0.20
Th	4.8	1.6	1.6	0.20
Yb	4.3	2.2	6.2	0.77
Cs	3.9	3.0	3.1	0.23
Hf	2.8	1.0	4.5	2.2
U	2.3	0.94	1.1	0.19
Eu	2.0	0.10	3.5	0.10
Ta	1.8	0.74	0.54	0.14
Tb	1.8	1.0	9.0	1.8
As	1.1	0.30	0.28	0.11
Sb	0.51	0.014	0.81	0.20
Se	0.050	0.52	0.60	0.32

TABLE 5
Site Concentrations for Top Samples

Top Only Site No.	element			short t%
	Mn (ppm)	Ti (ppm)	V (ppm)	Al (wt%)
	1226	3750	89.4	5.85
1	397	3670	670	4.35
2	377	5450	105	7.42
3	471	2580	64.0	4.52
4	155	3530	61.7	4.43
3A	973	3750	75.6	5.93
5	395	5430	97.8	6.53
7	266	2130	28.2	2.59
8	421	5220	103	8.52
9	639	4390	91.0	5.92
12	973	4330	88.1	5.83
13	1502	5700	139	10.3
14	429	3120	46.3	3.88
27A	568	5470	102	7.92
14A	981	7050	109	7.65
14B	1165	6500	136	9.47
25A	1289	1090	258	2.23
16	830	5030	88.4	7.01
15	660	2900	54.1	3.58
15A	968	4890	87.4	6.48
17	431	4910	74.2	5.83
18	374	4280	60.9	4.27
19	1714	5930	135	9.86
20	390	3040	38.1	3.46
20D	1277	4710	94.6	6.20
6	179	6190	190	12.9
10	853	6240	135	8.98
11	844	6470	140	8.64
7A	1169	6870	148	10.9
20A	1118	6280	167	10.9
26A	2192	5580	136	9.30
28A				

TABLE 6

site Concentrations for Top Samples (ppm)

Top Only Site No.	Na	Sc	Cr	Co	Rb
1	2520	12.7	64.8	12.2	111
1	4040	6.8	69.0	9.7	74.8
2	6190	11.7	66.4	13.7	101
3	5720	6.5	44.7	8.9	66.1
4	5200	6.2	44.8	7.7	62.7
3A	4860	8.4	46.9	11.8	99.9
5	5730	9.7	58.3	12.4	107
7	3570	3.3	26.9	4.6	33.1
8	1330	14.6	66.4	9.8	106
9	6080	8.7	44.9	12.0	89.8
12	5960	8.8	49.5	12.4	82.7
13	4130	17.0	89.8	23.3	175
14	5470	5.4	31.8	8.9	57.9
27A	5330	12.5	69.1	17.6	134
14A	5140	12.2	122.0	15.3	124
14B	4210	15.6	97.0	20.8	153
25A	2700	2.6	18.9	8.6	30.3
16	5790	11.3	63.4	15.4	107
15	4950	5.2	40.5	8.6	56.5
15A	5230	10.2	66.4	15.2	93.7
17	6480	9.5	59.7	11.7	95.5
18	5720	6.3	39.0	7.4	59.4
19	5290	15.4	78.4	21.5	160
20	7040	4.1	28.5	6.9	42.9
20D	5810	9.5	51.7	26.3	112
6	1510	22.7	96.8	8.4	152
10	5040	14.3	72.1	15.6	134
11	4690	14.0	77.2	17.6	128
7A	4380	18.4	90.0	22.7	183
20A	3840	18.6	95.3	23.5	179
26A	4880	14.6	72.7	20.4	144
28A					

TABLE 7
Site Concentrations for Top Samples (ppm)

Top Only Site No.	Ba	La	Sm	Yb	Lu
	330	37.1	6.44	3.26	0.45
1	340	26.9	4.90	3.25	0.44
2	386	38.2	7.12	3.40	0.46
3	285	24.7	4.88	2.58	0.35
4	334	25.6	5.04	2.82	0.42
3A	385	28.6	5.36	2.52	0.34
5	384	38.0	7.21	3.90	0.55
7	222	11.2	2.18	1.55	0.21
8	461	49.0	9.37	4.25	0.60
9	417	31.7	5.75	2.95	0.42
12	351	34.4	6.78	3.42	0.48
13	556	51.3	8.86	3.99	0.55
14	297	19.5	4.17	2.05	0.28
27A	475	41.0	7.44	3.51	0.51
14A	378	48.0	8.82	4.70	0.68
14B	558	52.0	9.13	4.13	0.61
25A	217	11.8	2.54	1.09	0.14
16	412	39.1	7.28	3.51	0.51
15	259	30.0	4.45	2.50	0.34
15A	387	36.0	6.71	3.16	0.45
17	363	36.3	6.31	3.45	0.48
18	251	21.5	4.04	2.77	0.41
19	480	46.7	8.06	3.71	0.52
20	259	18.6	3.86	2.16	0.32
20D	421	38.0	8.18	3.69	0.50
6	551	35.8	5.26	3.64	0.51
10	482	42.1	7.76	3.76	0.54
11	479	43.6	7.90	3.93	0.55
7A	597	52.0	9.01	3.96	0.56
20A	644	52.6	9.17	4.09	0.59
26A	512	45.2	8.07	3.99	0.54
28A					

TABLE 8

site Concentrations for Top Samples (ppm & wt%)

Top Only Site No.	Zn (ppm)	Cs (ppm)	Sb (ppm)	Ca (wt%)	Fe (wt%)
1	136	8.19	1.18	1.59	3.57
2	107	3.46	0.86	1.58	2.52
3	146	6.23	0.91	1.68	3.32
3A	89.8	2.67	0.56	1.21	1.20
4	110	3.01	0.95	1.17	2.12
5	118	3.88	0.95	1.25	2.54
7	163	4.70	2.16	1.66	2.59
8	56.1	1.34	0.56	0.70	1.13
9	133	5.08	0.81	1.89	3.52
12	113	3.73	0.64	1.44	3.05
13	118	4.09	0.77	1.48	2.60
14	252	8.80	1.95	1.93	4.67
14A	76.3	2.27	0.71	1.10	2.00
14B	190	6.60	1.93	1.76	3.65
25A	191	5.41	1.47	2.20	3.77
16	240	8.71	1.80	2.38	4.56
15	53.9	1.24	0.41	0.46	1.91
15A	168	5.44	1.88	1.87	3.38
17	87.4	1.98	1.45	1.18	2.17
18	154	5.04	1.32	1.76	3.31
19	130	5.04	1.12	1.74	3.37
20	76.7	3.00	0.53	1.38	2.00
20D	204	9.20	1.56	1.84	4.35
6	48.2	1.57	0.59	1.21	1.42
10	115	4.12	0.90	1.48	4.17
11	141	13.70	0.86	2.15	5.28
7A	163	6.58	1.12	1.73	3.86
20A	209	7.93	1.90	1.84	3.92
26A	227	10.79	2.04	1.87	5.01
28A	281	11.78	2.13	2.09	5.07
	238	7.90	2.37	2.03	4.00

TABLE 9
Site Concentrations for Top Samples (ppm)

Top Only Site No.	Th	Nd	U	As
	10.00	28.3	3.77	22.5
1	7.07	22.3	2.65	10.8
2	10.53	34.9	2.94	20.4
3	6.53	28.6	2.22	6.0
3A	6.50	25.6	2.24	13.0
4	7.59	26.4	2.48	14.4
5	9.83	32.1	3.44	13.0
7	3.14	8.0	1.26	6.3
8	13.60	44.4	4.74	6.2
9	8.83	30.3	2.77	19.0
12	9.00	25.8	2.90	14.8
13	13.33	52.3	3.91	23.7
14	5.17	15.4	1.67	13.6
27A	11.41	38.3	3.25	19.2
14A	13.30	32.8	4.02	18.6
14B	13.02	39.9	4.14	20.4
25A	2.94	9.3	1.04	21.4
16	10.68	30.6	3.25	18.9
15	5.80	17.4	2.04	14.3
15A	9.22	26.3	3.07	15.0
17	9.67	33.1	3.30	25.6
18	6.10	16.6	2.27	9.6
19	12.40	39.6	3.84	24.2
20	4.86	15.7	2.05	11.6
20D	9.21	40.8	3.27	23.3
6	15.23	28.0	4.56	9.9
10	12.07	37.3	3.88	19.0
11	11.97	43.4	3.39	20.3
7A	13.82	39.1	4.28	28.8
20A	14.18	53.7	4.04	25.5
26A	12.13	42.8	3.60	22.3
28A				

TABLE 10: Mn (ppm)

site No.	Top	Middle	Bottom
4	471	1091	531
6	1277	193	5350
10	179	228	4180
11	853	128	134
7A	844	660	1140
20A	1169	497	453
26A	1118	743	1260
28A	2192	880	867
14	1502	695	943

NOTE:

The letter A after the site number indicates the site is a river channel site.

No letter after number indicates a tributary or lake bed site.

TABLE 11: V (ppm)

Site No.	Top	Middle	Bottom
4	64.0	96.8	40.3
6	94.6	85.1	99.8
10	190	190	113
11	135	153	169
7A	140	36	109
20A	148	33.7	79
26A	167	171	69
28A	136	123	94.4
14	139	175	172

TABLE 12: Ti (ppm)

Site No.	Top	Middle	Bottom
4	3580	4060	5080
6	4710	3940	5330
10	6190	5360	3630
11	6240	7740	6810
7A	6470	3740	4900
20A	6870	6230	4250
26A	6280	6190	6200
28A	5580	5510	5680
14	5700	6020	4800

TABLE 13: Al (wt%)

site No.	Top	Middle	Bottom
4	4.52	6.63	6.95
6	6.20	6.55	5.66
10	12.9	13.2	7.08
11	8.98	13.3	13.4
7A	8.64	5.53	7.20
20A	10.9	11.1	5.21
26A	10.9	9.77	4.87
28A	9.30	7.42	6.44
14	10.3	9.33	10.9

TABLE 14: Na (ppm)

Site No.	Top	Middle	Bottom
4	5720	5790	6120
6	5810	5670	5370
10	1510	1690	896
11	5040	1580	1580
7A	4690	5130	4740
20A	4380	3890	5710
26A	3840	4290	4150
28A	4880	5290	5100
14	4130	4150	4140

TABLE 15: Sc (ppm)

Site No.	Top	Middle	Bottom
4	6.5	10.1	10.9
6	9.5	10.0	9.6
10	22.7	21.4	17.6
11	14.3	19.9	20.2
7A	14.0	9.2	13.1
20A	18.4	18.3	8.9
26A	18.6	16.9	17.8
28A	14.6	13.2	11.5
14	17.0	17.8	18.3

TABLE 16: Cr (ppm)

Site No.	Top	Middle	Bottom
4	44.7	60.5	62.7
6	51.7	53.4	50.5
10	96.8	88.8	70.3
11	72.1	93.7	90.5
7A	77.2	50.8	75.1
20A	90.0	89.9	55.1
26A	95.3	90.5	97.4
28A	72.7	79.9	62.3
14	89.8	89.8	95.8

TABLE 17: Co (ppm)

site No.	Top	Middle	Bottom
4	8.9	13.6	13.3
6	26.3	7.7	47.1
10	8.4	9.8	26.4
11	15.6	5.0	4.7
7A	17.6	15.0	23.8
20A	22.7	18.2	13.7
26A	23.5	27.4	24.2
28A	20.4	21.0	18.7
14	23.3	23.1	26.3

TABLE 18: Rb (ppm)

Site No.	Top	Middle	Bottom
4	66.1	102	114
6	112	103	101
10	152	176	106
11	134	175	175
7A	128	96.4	147
20A	183	199	99.3
26A	179	196	198
28A	144	135	132
14	175	193	184

TABLE 19: Ba (ppm)

site No.	Top	Middle	Bottom
4	285	392	422
6	422	445	570
10	551	368	298
11	482	605	496
7A	479	391	602
20A	597	595	373
26A	644	549	759
28A	512	567	451
14	556	709	604

TABLE 20: La (ppm)

Site No.	Top	Middle	Bottom
4	24.7	36.6	38.6
6	38.0	35.5	41.4
10	35.8	34.2	32.8
11	42.1	41.0	45.3
7A	43.6	32.2	42.9
20A	52.0	49.6	36.2
26A	52.6	50.1	51.2
28A	45.2	42.0	37.8
14	51.3	51.4	51.9

TABLE 21: Sm (ppm)

site No.	Top	Middle	Bottom
4	4.88	7.16	7.20
6	8.18	7.13	8.51
10	5.26	6.74	5.54
11	7.76	5.02	5.62
7A	7.90	6.09	7.92
20A	9.01	8.67	7.25
26A	9.17	8.63	8.93
28A	8.07	7.78	6.76
14	8.86	8.66	8.98

TABLE 22: Yb (ppm)

Site No.	Top	Middle	Bottom
4	2.58	3.83	4.36
6	3.69	2.73	3.09
10	3.64	3.25	2.53
11	3.76	4.21	4.58
7A	3.93	3.19	3.79
20A	3.96	4.20	4.04
26A	4.09	4.04	4.31
28A	3.99	4.17	3.38
14	3.99	4.46	4.35

TABLE 23: Lu (ppm)

Site No.	Top	Middle	Bottom
4	0.35	0.56	0.59
6	0.50	0.40	0.44
10	0.51	0.46	0.37
11	0.54	0.63	0.68
7A	0.55	0.44	0.53
20A	0.56	0.56	0.53
26A	0.59	0.59	0.56
28A	0.54	0.60	0.47
14	0.55	0.60	0.57

TABLE 24: Th (ppm)

Site No.	Top	Middle	Bottom
4	6.50	9.95	10.45
6	9.21	9.49	9.69
10	15.23	14.54	9.93
11	12.07	14.42	15.11
7A	11.97	8.33	11.62
20A	13.82	13.46	9.68
26A	14.18	13.36	13.48
28A	12.13	11.51	10.24
14	13.33	13.88	13.97

TABLE 25: Nd (ppm)

Site No.	Top	Middle	Bottom
4	25.6	33.9	40.0
6	40.8	48.7	48.0
10	28.0	48.9	40.0
11	37.3	38.9	43.8
7A	43.4	28.4	52.9
20A	39.1	68.7	40.6
26A	53.7	42.0	49.5
28A	42.8	44.3	48.6
14	52.3	69.5	70.1

TABLE 26: U (ppm)

site No.	Top	Middle	Bottom
4	2.24	3.14	3.28
6	3.27	2.81	2.97
10	4.56	4.17	3.58
11	3.88	5.20	4.71
7A	3.39	2.82	3.26
20A	4.28	3.93	2.97
26A	4.04	3.65	3.42
28A	3.60	3.56	3.15
14	3.91	3.93	3.67

TABLE 27: As (ppm)

Site No.	Top	Middle	Bottom
4	13.0	17.0	16.4
6	23.3	12.5	25.0
10	9.9	12.3	35.5
11	19.0	3.9	11.6
7A	20.3	14.7	22.2
20A	28.8	17.9	10.1
26A	25.5	21.1	24.4
28A	22.3	18.9	17.6
14	23.7	19.9	22.8

TABLE 28: Zn (ppm)

Site No.	Top	Middle	Bottom
4	110	141	139
6	115	114	149
10	141	129	181
11	163	168	192
7A	209	155	232
20A	227	271	121
26A	281	282	274
28A	238	213	182
14	252	280	294

TABLE 29: Cs (ppm)

Site No.	Top	Middle	Bottom
4	3.01	4.99	5.81
6	4.12	4.13	4.74
10	13.70	13.37	6.76
11	6.58	14.72	12.46
7A	7.93	4.76	7.56
20A	10.79	9.87	3.93
26A	11.78	9.04	10.09
28A	7.90	6.76	5.38
14	8.80	9.32	10.70

TABLE 30: Sb (ppm)

Site No.	Top	Middle	Bottom
	1.17	1.83	1.68
4	0.95	0.99	0.93
6	0.90	0.63	0.90
10	0.86	1.02	1.11
11	1.12	0.68	0.66
7A	1.90	1.16	1.71
20A	2.04	2.47	0.60
26A	2.13	2.32	2.22
28A	2.37	1.99	1.68
14	1.95	2.19	2.77

TABLE 31: Ca (wt%)

site No.	Top	Middle	Bottom
4	1.17	1.63	1.68
6	1.48	1.56	1.45
10	2.15	2.14	1.21
11	1.73	2.55	2.44
7A	1.84	1.58	1.92
20A	1.87	1.92	1.57
26A	2.09	2.02	1.96
28A	2.03	1.92	1.59
14	1.93	2.08	2.03
14	4.67	4.60	4.85

TABLE 32: Fe (wt%)

TABLE 33: Top Only - 40 day (all ppm)

Site No.	Top	Middle	Bottom
4	2.12	2.98	2.88
6	4.17	2.60	4.77
10	5.28	5.91	28.90
11	3.86	1.66	1.97
7A	3.92	2.62	4.05
20A	5.01	4.82	2.19
26A	5.07	4.40	4.77
28A	4.00	3.60	3.33
14	4.67	4.60	4.85

TABLE 33: Top Only - 40 day (all ppm)

Site No.	Zr	Hf	Ta	Ni	Ce
4	294	9.1	0.6	21.6	55.0
6	414	11.2	0.9	26.3	86.3
10	365	7.2	1.3	32.5	68.4
11	354	9.8	1.0	39.2	90.2
7A	397	9.5	1.1	27.8	94.6
20A	262	6.6	1.2	39.9	110
26A	322	6.3	1.4	37.6	112
28A	262	8.4	1.3	34.3	93.3
14	289	7.0	1.2	40.9	107

TABLE 34: Top Only - 40 day (all ppm)

From Experimental Data - Std. Dev.

Site No.	Eu	Tb	Se	Sr			
Element	Top Std. Dev.	Middle Std. Dev.	Bottom Std. Dev.				
4 Nd	0.92	54.7	0.60	49.3	1.2	101	103
Ti	15.7			19.8		18.0	
6 V	1.47	1110	1.03	1260	2.1	1210	118
Al	0.26			0.35		0.23	
10 Ba	0.99	312	1.16	253	2.8	255	153
Sc	0.5			0.7		0.7	
11 Cr	1.36	7.4	1.03	9.3	2.0	8.8	126
Co	1.2			1.5		1.9	
7A Nb	1.45	13.3	1.04	19.6	3.2	19.0	98.8
Ba	64.7			88.4		88.8	
20A La	1.64	2.0	0.99	2.4	3.8	2.4	136
Sm	0.48			0.54		0.54	
26A Yb	1.67	0.37	1.21	0.44	2.8	0.4	215
La	0.07			0.08		0.08	
28A Th	1.44	0.68	0.91	0.85	3.0	0.8	201
Nd	8.0			13.6		13.9	
14 U	1.56	0.52	1.17	0.50	2.6	0.5	130
As	1.6			1.4		1.8	
Zn	16.4			21.4		21.8	
Cs	0.62			0.97		0.94	
Sb	0.20			0.24		0.23	
Ca	0.17			0.20		0.19	
Fe	0.16			0.18		0.31	
Hu	0.13			---		---	
Tb	0.13			---		---	
Se	1.1			---		---	
Ni	17.2			---		---	
Sr	57			---		---	
Zr	97			---		---	
Hf	0.5			---		---	
Ta	0.2			---		---	
Ce	4.9			---		---	

TABLE 35

From Experimental Data - Std. Dev.

Element	Top Std. Dev.	Middle Std. Dev.	Bottom Std. Dev.
Mn	54.7	49.3	101
Ti	15.7	19.8	18.0
V	1110	1260	1210
Al	0.26	0.35	0.29
Na	312	253	255
Sc	0.5	0.7	0.7
Cr	7.4	9.3	8.8
Co	1.2	1.5	1.9
Rb	13.3	19.6	19.0
Ba	64.7	88.4	88.8
La	2.0	2.4	2.4
Sm	0.48	0.54	0.54
Yb	0.37	0.44	0.45
Lu	0.07	0.08	0.08
Th	0.68	0.85	0.81
Nd	8.0	13.6	13.9
U	0.52	0.60	0.56
As	1.6	1.4	1.8
Zn	16.4	21.4	21.8
Cs	0.62	0.97	0.94
Sb	0.20	0.24	0.23
Ca	0.17	0.20	0.19
Fe	0.16	0.18	0.31
Eu	0.13	---	---
Tb	0.13	---	---
Se	1.1	---	---
Ni	17.2	---	---
Sr	57	---	---
Zr	97	---	---
Hf	0.5	---	---
Ta	0.2	---	---
Ce	4.9	---	---

TABLE 36: Soil 5 From Top Data

Element	Exp.Conc.	Stated.Conc.	% error
Al	10.67	8.19	30.28
Mn	804.52	852	5.57
V	176.90	151	17.15
Ti	5500	4700	17.12
Na	19900	19200	3.71
Sc	14.68	14.8	0.81
Cr	31.98	28.9	10.66
Fe	4.39	4.45	0.30
Co	14.67	14.8	0.88
Rb	147.31	138	6.75
Ba	535.01	562	4.80
La	27.43	28.1	2.38
Sm	5.46	5.42	0.74
Yb	2.32	2.24	3.57
Lu	0.330	0.336	1.78
Th	11.71	11.3	3.63
Nd	29.67	29.9	0.77
U	3.54	3.15	12.38
As	92.24	93.9	1.77
Ca	2.24	2.20	1.82
Zn	355.34	368	3.44
Cs	57.61	56.70	1.60
Sb	15.45	14.30	8.04
Eu	1.20	1.18	1.69
Tb	0.660	0.665	0.75
Se	1.05	1.3	19.23
Sr	325.22	330	1.45
Zr	168.89	221	23.58
Hf	6.08	6.3	3.49
Ta	0.770	0.764	0.78
Ce	58.37	59.7	2.23
Ni	20.09	13.0	54.54

$$\% \text{ error} = \frac{|\text{exp.conc.} - \text{stated conc.}|}{\text{stated conc.}} \times 100$$

TABLE 37: Soil 5 From Middle & Bottom Data

Element	Exp.Conc.	Stated Conc.	% error
Al	10.47	8.19	27.83
Mn	917.96	852	7.74
V	165.50	151	9.60
Ti	4620	4700	1.75
Na	19100	19200	0.56
Sc	14.65	14.8	1.01
Cr	29.89	28.9	3.42
Fe	4.37	4.45	1.80
Co	14.33	14.8	3.18
Rb	122.22	138	11.43
Ba	649.05	562	15.49
La	27.13	28.1	3.45
Sm	5.28	5.42	2.58
Yb	2.10	2.24	6.25
Lu	0.340	0.336	0.12
Th	9.76	11.3	13.63
Nd	26.90	29.9	10.03
U	3.07	3.15	2.54
As	93.44	93.9	0.49
Ca	2.22	2.20	0.91
Zn	376.05	368	2.19
Cs	57.61	56.70	1.60
Sb	14.38	14.30	0.56

TITANIUM

$$\% \text{ error} = \frac{|\text{exp. conc.} - \text{stated conc.}|}{\text{stated conc.}} \times 100$$

MANGANESE

From Table 4, Mn is found to be a fairly common metallic element in the rocks and minerals of the earth, but there is only about 1/50th as much Mn in the earth as there is Fe. Even though Mn is fairly abundant, it is not an essential component of the more common silicate rocks and minerals.

Mn is often present in streams that receive drainage from coal mines and is usually carried further downstream from a pollution source than Fe.¹⁴

From the data, the measured concentrations vary from 128 to over 5000 ppm. The bottom samples of sites 6 and 10, and the top sample of site 28A contain the highest concentration of Mn.

TITANIUM

Although Ti is one of the more abundant elements found in the rocks and minerals of the earth, it is usually present in water in very low concentration.¹⁵

The oxide is used as a white pigment in paint and metallic Ti is used extensively in the space and aircraft industries. Both of these uses of this element can artificially increase the amount of Ti in certain regions, but as mentioned earlier, Ti is common and widely distributed throughout the earth and can be readily available without man's influence. Ti may also be associated with brine.¹⁵

From the collected data, it is seen that the concentrations vary from 1000 to 7000 ppm (with an error of +/- 1200 ppm). The sites with the highest concentrations are 14B (top), 11 (middle and bottom), and site 20A (top).

VANADIUM

V is fairly abundant in the earth. V is found to be present in plants and in coal. It is also present in petroleum products, and combustion of these products releases higher amounts of V into the environment.¹⁶

The measured concentrations of V range from 25 to 189 ppm. The highest concentrations are found in the top and middle samples of site 10.

The data obtained from the top samples shows that sites 20B, 18, 13, and 11 have the highest concentrations of V.

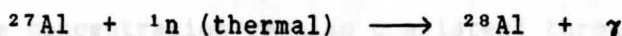
ALUMINUM

Al is the second most abundant element in the earth's crust following Si (excluding O, which is the most abundant). Al occurs in many rock and minerals; the most common mineral Al is found in is clays.

From Tables 36 and 37, the percent error for Al measured in the standard, soil-5, is greater than 25%. It should be noted that Al measurements by NAA are inherently inaccurate. This is because the Al-28 isotope that is formed from thermal neutron bombardment is also formed from Si-28 by an (n,p) reaction with fast neutrons. When using the rabbit facility, the total flux contains about 29-30% fast

Cr is found in rocks and minerals, but is also a pollutant from industries associated with steel manufacturing. Sites 14B, 20A, 10,

neutrons. Since this occurs, contributions from the (n,p) reaction are bound to occur.



SODIUM

Na is fairly abundant in the earth's crust, but human activities can also have a direct effect on the concentration of Na in a particular region. Brine from oil wells, the use of salt on roads during winter, and sewage contamination can dramatically increase the concentration of Na.¹⁷

The data shows there is a wide variance in the concentration of Na as a result of contamination. The data obtained from the top samples shows that sites 20D, 18, 13, and 12 have the highest concentrations of Na. The data for the top, middle, and bottom samples of the nine chosen sites indicates that the concentration of Na is consistent throughout most sites except sites 11 and 20A.

SCANDIUM

The data for Sc seems to agree with the values listed for Sc in Table 4. The sites containing the highest concentration of Sc are sites 10, 26A, and 20A.

CHROMIUM

Cr is found in rocks and minerals, but is also a pollutant from industries associated with steel manufacturing. Sites 14B, 25A, 10,

and 26A have the highest concentrations in the top samples of these sites. The concentration of Cr increases as a function of depth for site 11, and the concentration remains consistent throughout for sites 14 and 26A (which are also the highest).

COBALT

Co is present in the earth's crust as a minor constituent. Co is used in the making of steel alloys, where it is often combined with Cr. The concentrations for the top, middle, and bottom samples of the river channel sites and site 14 remain fairly consistent throughout.

The bottom sample for site 6 is the highest compared to all, indicating contaminants. For site 10, the top and middle samples are low, but the bottom sample is higher. The opposite is so for site 11, where the top sample has the highest concentration.

RUBIDIUM

Rb is fairly abundant in the earth as indicated by Table 4.

The measured concentrations vary from 30 to 198 ppm, indicating Rb is not equally distributed throughout the region. This may be due to different types of rocks and minerals present in this regional area. Rb is also found in the ash of a number of plants, such as beet, oak, tea, and tobacco.¹⁸ The top samples from sites 8 and 16 contain the lowest concentration, whereas the middle samples of sites 26A and 14 and the bottom sample of site 26A contain the highest concentration of Rb.

BARIUM

Ba is found to be abundant in the rocks and minerals of the earth's crust. From the data, the concentrations range from 217 to above 750 ppm, with the highest values in the middle sample of site 14 and the bottom sample of site 26A. Other than this, the concentrations are fairly consistent. High Ba concentrations can be found in oil fields and brines.¹⁹

LANTHANUM

La is a minor constituent found in the earth. La is used in glazes for ceramic and glass.²⁰ From the data obtained, the concentrations vary from 11 to 52 ppm. The top samples of sites 8 and 16 contain the smallest concentration. Sites 26A and 14 contain the highest concentration throughout top, middle, and bottom.

SAMARIUM

Sm is another minor constituent found in the earth. The measured concentrations vary from 4-9 ppm indicating that Sm is fairly consistent throughout the regional area. The sites containing the highest concentration of Sm are the tops of 3 river channel sites, 20A, 26A and 25A.

YTTTERBIUM

Yb is a minor constituent of the earth. The measured concentrations range from 1 to 4 ppm indicating Yb is consistent

throughout the area. The sites containing the greatest amounts of Yb are 14B (top), 14 (middle), and the bottom of sites 11 and 14.

LUTETIUM

Lu is one of the least abundant elements found in the earth; it is found naturally in concentrations of 0.1 to about 1 ppm. From the data, it is seen that Lu varies from 0.1 to no greater than 0.7 ppm. Looking at the data for the top, middle and bottom samples of the nine chosen sites, the concentration seems to be consistent throughout.

ZINC

Zn has about the same abundance in rocks and minerals as Ni, and it is therefore fairly common. Zn is used widely in industry, in metallurgy, and for galvanizing steel. It is also widely used as a white pigment (zinc oxide) in rubber and paint. Another point of interest is that Zn concentrations are increased in streams affected by mine drainage. These applications tend to disperse the element widely throughout the environment.²¹ The sites with the highest concentrations are sites 26A (top, middle and bottom) and the middle and bottom of site 14.

CESIUM

Cs is found not to be very abundant in the earth. Igneous rocks contain the highest concentration of 4.3 ppm. A use for Cs is in photoelectric cells.²² From the data, it is noticed that the

concentrations range from 1 to 14 ppm, with the highest values found in site 10 (top, middle and bottom) and the middle sample of site 11.

concentration of Fe, most notably the bottom sample.

ANTIMONY

Sb is one of the least abundant of all elements found in the rocks and minerals of the earth. Igneous rocks contain 0.51 ppm and shale, 0.81 ppm. From the data, the concentrations range from 0.4 to well above 2 ppm. The sites containing the highest concentrations of Sb are site 26A (middle and bottom), the top of site 28A, and the bottom of site 14. Mine drainage water may contain higher amounts of Sb that may settle out into the surrounding sediment.²³ Sb is also used in electroplating and in the making of fireworks and matches, as well as in steel manufacturing.²⁴

Nd is more abundant in the earth than Th and U, but it is still a relatively minor constituent. The data obtained indicates that

CALCIUM

sites 14 (middle and bottom) and the middle sample of site 20A contain

the highest. Ca is the most abundant of the alkaline earth metals found in the earth. It is a major constituent of many common rocks and minerals. The data indicates that the Ca concentration is fairly consistent throughout the area, where site 16 (top) contains the smallest concentration and site 11 (middle and bottom) contains the highest.

U is found naturally in the rocks and minerals of the earth's crust, it also occurs in smaller quantities than Th. The measured concentrations vary from 1.04 to 5.26 ppm, indicating that the element seems to be fairly consistent throughout the area.

IRON

Fe is the second most abundant metallic element found in the earth's outer crust. It is found mainly in igneous rocks and minerals. Fe is also a contaminant from steel industries and higher

concentrations of Fe are found in water and sediments that are drained from coal mines.²⁵ All three samples of site 10 contain the highest

concentration of Fe, most notably the bottom sample.

THORIUM

Th occurs naturally in rocks and sediments, and from Table 4, it is seen that Th is more abundant than U. Also, in some types of rocks and minerals Th may occur in association with U.²⁶ From the data obtained, it is seen that the concentrations vary from about 3 to 15 ppm, which seems to agree with the values listed in Table 4.

NEODYMIUM

Nd is more abundant in the earth than Th and U, but it is still a relatively minor constituent. The data obtained indicates that sites 14 (middle and bottom) and the middle sample of site 20A contain the highest amounts of Nd.

URANIUM

U is found naturally in the rocks and minerals of the earth's crust, it also occurs in smaller quantities than Th. The measured concentrations vary from 1.04 to 5.20 ppm, indicating that the element seems to be fairly consistent throughout the area.

ARSENIC

From Table 4, it is seen that As is one of the elements of lowest concentration found in the earth. Because small amounts of As can be toxic to human life, it is considered a highly undesirable contaminant. Over the years As has been used in pesticides, and it can therefore enter streams through agricultural drainage or from waste disposal. As also has been used in various paints, and it can also be released in the burning of coal.²⁷ From Table 4, the highest value listed for As is 9.0 ppm. From the data obtained for the nine selected sites, the highest value is 35.52 ppm. It can be seen from the data for the selected sites, with a few exceptions, most values are greater than 9.0 ppm. Site 10 (bottom) has the highest concentration.

THE REMAINING ELEMENTS

The nine remaining elements (Zr, Hf, Ta, Ni, Ce, Eu, Tb, Se, and Sr) have the longest half-lives and were not measured until a decay period of 40 days had passed. The measurements were made on the top samples of the nine chosen sites. The same measurements were not done on the middle and bottom samples of these sites because as mentioned earlier, the OSU-NRL temporarily closed down and the 40 day analysis overlapped into this period. Of these elements, Zr, Ce, and Sr, are all relatively abundant naturally. In Table 4 the highest concentration of Zr is 204 ppm, whereas sites 6 and 7A have values of about 400 ppm (+/- 97 ppm). The measured concentrations for Ce, with the exception of sites 4 and 10

(which are lower), are relatively consistent. The values for Sr are all relatively consistent except for two sites, which have higher values, sites 26A and 28A.

The chemistry of Sr is very similar to that of Ca. Sr is a fairly common element, sometimes replacing Ca in certain rocks and minerals in minor amounts. The sites with the highest amounts of Sr are sites 26A and 28A, where the higher amounts can be attributed to the dissolution of many rocks and minerals.¹⁹

Ni is a minor constituent in the earth's crust. It is an important industrial metal. Ni is used in stainless steel and other alloys that are corrosion resistant. Because of its extensive uses, Ni can be introduced into the environment in large amounts by waste disposal. Sites 14, 11, and 20A have the highest measured concentrations of Ni.

Eu, Ta, Hf, and Tb are all present naturally in very small quantities. The measured values of the nine sites for Eu, Ta, and Tb are all relatively consistent throughout for each element. The data obtained for Hf varies from 6 to 11 ppm, higher than the values listed in Table 4.

Se is the least abundant of the elements listed in Table 4. The measured values for Se range from 1 to just under 4 ppm, again higher than the values listed in Table 4 (even with an error of +/- 1.09 taken into account). Some plant species have been found to contain several thousand mg of Se per kg of dry plant parts because these plants are noted for accumulating Se from the soil by taking it up through their root systems.²³ This may be a reason for the higher concentrations of Se detected in the sediment samples compared to the

values listed in Table 4. An interesting note is that the Youngstown area was reported to be a low Se area (one where the grass and foilage contain up to 0.05 ppm) in 1973. A report in the Medical Tribune from that year (which did soil studies on various U.S. cities) states that cancer incidence is not so great when there is plenty of Se in the soil.²⁸

Table 38 lists their results. By comparison, the mean of the following elements are higher than the mean listed by the above authors: Al, Ti, Fe, As, Ba, Co, Cr, Cs, Nb, Sc, Th, and V. Of the other elements analyzed in the sediments taken from the Lake Milton bed and tributaries, the mean values are all about the same or slightly lower than the listed values reported in Table 38.

The 12 elements listed above are one and one-half times to as great as four times higher than the mean values listed in the Madkari and Morrison table. The mean for Th is higher than the mean values reported by the two authors, however based on the results obtained for all sites. Th seems to be naturally higher in this particular region. Al may seem to be high due to the large error associated with analyzing it by NAA. The mean for Sc found in the samples is greater than the mean listed in Table 38, however the measured concentration of Sc seems to agree with Table 4. This seems to indicate that Sc is naturally higher in this area when compared to the Madkari and Morrison study. Nb is three to four times higher than the mean listed in Table 38. The variance in the measured concentrations may be due to the different types of minerals in this area and may also possibly be due to the different types of plants in this area.

CHAPTER V

Data of Nadkarni and Morrison (ref 29)
Units in CONCLUSIONS AND DISCUSSION

Data from a lake sediment analysis (by NAA) by Nadkarni and Morrison were used for comparison.²⁹ They determined the concentration ranges of trace elements in a relatively pollution free lake. Table 38 lists their results. By comparison, the mean of the following elements are higher than the mean listed by the above authors: Al, Ti, Fe, As, Ba, Co, Cr, Cs, Rb, Sc, Th, and V. Of the other elements analyzed in the sediments taken from the Lake Milton bed and tributaries, the mean values are all about the same or slightly lower than the listed values reported in Table 38.

The 12 elements listed above are one and one-half times to as great as four times higher than the mean values listed in the Nadkarni and Morrison table. The mean for Th is higher than the mean values reported by the two authors, however based on the results obtained for all sites, Th seems to be naturally higher in this particular region. Al may seem to be high due to the large error associated with analyzing it by NAA. The mean for Sc found in the samples is greater than the mean listed in Table 38, however the measured concentration of Sc seems to agree with Table 4. This seems to indicate that Sc is naturally higher in this area when compared to the Nadkarni and Morrison study. Rb is three to four times higher than the mean listed in Table 38. The variance in the measured concentrations may be due to the different types of minerals in this area and may also possibly be due to the different types of plants in this area.

TABLE 38

Data of Nadkarni and Morrison (ref 29)
Units in ppm unless otherwise stated

Element	Range	Mean
Al (wt%)	2.62-6.38	4.38
Ti	800-3800	2800
Na	3000-9200	6100
Ca (wt%)	1.23-4.00	2.69
Fe (wt%)	1.47-3.06	2.24
La	28-73	37
Ce	53-160	85
Nd	15-137	52
Sm	7.86-28	13
Eu	0.77-1.94	1.28
Tb	0.95-2.39	1.52
Yb	2.34-9.34	4.46
Lu	0.52-1.20	0.72
As	1.86-26	13
Ba	163-375	287
Co	3.91-16	7.31
Cr	16-50	27
Cs	0.56-14	2.93
Hf	1.67-12	7.05
Mn	214-4500	684
Ni	<1-218	38
Rb	19-49	35
Sb	<0.01-2.9	1.56
Sc	3.30-9.16	5.70
Se	0.03-1.01	0.39
Sr	<10-242	90
Ta	0.41-1.44	0.87
Th	4.02-9.38	6.39
U	0.78-4.35	2.25
V	28-68	46.0
Zn	<10-450	278.0
Zr	54-488	263

These nine (9) elements were not analyzed in the middle and bottom samples due to lack of time.

TABLE 39: Top Samples

Units in ppm unless otherwise stated

Element	Range	Mean
Al (wt%)	2.23-12.86	6.82
Ti	1100-7050	4760
Na	1340-7040	4800
Ca (wt%)	0.46-2.38	1.60
Fe (wt%)	1.13-5.28	3.23
La	11-53	35
Ce*	55-112	91
Nd	8-54	31
Sm	2.18-9.37	6.52
Eu*	0.92-1.67	1.40
Tb*	0.60-1.21	1.02
Yb	1.09-4.70	3.28
Lu	0.14-0.68	0.46
As	6-29	17
Ba	217-644	402
Co	4.6-26.3	13.9
Cr	18.9-122	62.7
Cs	1.2-13.7	5.6
Hf*	6.3-11.2	8.3
Mn	155-2190	814
Ni*	21.6-40.9	33.3
Rb	30-183	105
Sb	0.41-2.37	1.24
Sc	2.6-22.7	10.9
Se*	1.2-3.8	2.6
Sr*	98.8-215	142
Ta*	0.65-1.4	1.1
Th	2.94-15.23	9.65
U	1.04-4.74	3.10
V	25.8-190	96.0
Zn	48.2-281	146
Zr*	261-414	329

* These nine (9) elements were not analyzed in the middle and bottom samples due to lack of time.

TABLE 40: Middle Samples

Units in ppm unless otherwise stated

Element	Range	Mean
Al (wt%)	5.53-13.31	9.20
Ti	3740-7740	5420
Na	1580-5790	4160
Ca (wt%)	1.56-2.55	1.93
Fe (wt%)	1.66-5.91	3.69
La	32-51	41
Nd	28.4-69.5	47.0
Sm	5.02-8.67	7.32
Yb	2.73-4.46	3.79
Lu	0.40-0.63	0.54
As	3.9-21.1	15.4
Ba	368-709	513
Co	5.0-27.4	15.7
Cr	50.7-93.7	77.5
Cs	4.1-14.7	8.6
Mn	128-1090	568
Rb	96.4-200	153
Sb	0.63-2.47	1.49
Sc	9.2-21.4	15.2
Th	8.33-14.54	12.10
U	2.81-5.20	3.69
V	33.7-190	118
Zn	17.3-26.7	21.4

TABLE 41: Bottom Samples

Units in ppm unless otherwise stated

Element	Range	Mean
Al (wt%)	4.87-13.36	7.52
Ti	3630-6810	5190
Na	896-6120	4200
Ca (wt%)	1.21-2.44	1.76
Fe (wt%)	1.97-28.9	6.41
La	32.8-51.9	42.0
Nd	40.0-70.1	48.2
Sm	5.54-8.98	7.41
Yb	2.53-4.58	3.82
Lu	0.37-0.68	0.53
As	10.1-35.5	20.6
Ba	298-759	508
Co	4.7-47.1	22.0
Cr	50.5-97.4	73.3
Cs	3.9-12.5	7.5
Mn	134-5350	1650
Rb	99.2-198	153
Sb	0.60-2.77	1.40
Sc	8.9-20.2	14.1
Th	9.68-15.11	11.57
U	2.97-4.71	3.44
V	40.3-172	105
Zn	17.4-27.3	21.8

Before the lake was filled in 1917, there were a few oil wells along the river that were pumped for the high quality oil present in small pockets. When the lake was filled, the water covered the wells and wiped out the industry there.³⁰ However, even after the lake was there, different corporations would still drill for oil and natural gas in that region, even into the 1980's.^{31, 32}

There are four elements associated with the drilling of oil wells. Higher concentrations of Ti, Na, and Ba are found in the brine from oil wells, and higher concentrations of V may be due to the fact that this element is found in petroleum products.

There are also several abandoned mine shafts in the Lake Milton area.³³ All but one are located to the west of the lake. There is one abandoned mine shaft that is in the area encompassing the sites in the Canyon Park area, sites 9, 10, 11, and 12. This shaft is still open and the people in that area are using it as a dump site.³³

There are four elements whose concentrations are dramatically increased by the water drainoff from this shaft. These elements are Mn, Zn, Sb, and Fe. This may explain why the bottom portion of site 10 had a measured concentration of 29 wt.% for Fe. Co and Cr may be associated with the presence of trash in the abandoned shaft, especially if there are numerous metal cans present. Ti is often found in the drainoff if the water is acidic.¹⁵ Cs concentrations were also the highest in sites 10 and 11.

Throughout the years, Lillian Drive (near site 13), Craig Beach, and the area on the southern shore of the lake (the trailer park) have had many problems with sewage and sewage disposal.^{34, 35} Na is the element most often associated with sewage. Site 20D was

located near a concrete retaining wall for cottages and it had the highest concentration of Na of all the samples measured. It was later discovered that the so-called indoor plumbing in those cottages was not that at all, but rather just pipes that went beneath the concrete slab upon which the cottages were sitting and that dumped the sewage directly into the Lake.³⁶

In 1974 there was a major fire in a plant in Alliance, and as a result chemical pollutants were dumped into Berlin Reservoir which then fed Lake Milton. As a result, both lakes were closed down for a few days, and even a few weeks later people were warned not to eat the fish caught from the two lakes.³⁷ The Alliance company handled such products as pesticides, farm chemicals, and various paints. Ti and As are used in paints, As is also used in pesticides. Since the area around Lake Milton is mainly agricultural, As may also be introduced into the lake by waste disposal or by drainage from the agricultural fields.

There are also elements that are consistent (or fairly consistent) throughout the regional area. These elements include Sm, Yb, Lu, Ca, U, Eu, Ta, Tb, Hf, Ce, and Sr.

Ti, Fe, As, Ba, Co, Cr, Cs, and V were found in the lake sediments in elevated concentrations. Co, Cr, V, Fe, Ba, and Ti could be contaminants from industrial sources. As and Ti could be contaminants from paints, and higher concentrations of As can also possibly result from agricultural use throughout the area. Sites in the Canyon Park residential area contained elevated concentrations of Fe, Co, Cr, Cs, and Ti which may be due to the presence of an abandoned mine shaft, which has been used as an illegal dump site.

Contamination from paints, a dumpsite, industry, etc. is a speculative rationale as to why the eight elements listed above are higher in concentration in Lake Milton when compared to the lake cited in ref. 29. Although the concentrations of these eight elements are greater, and in some cases much greater, than the values determined by Nadkarni and Morrison, the relatively large experimental errors in concentrations determined at both locations do not allow definite conclusions concerning the degree of pollution in the Lake Milton bed. This is due in part to the fact that a relatively small number of samples was taken from such a large heterogenous system.

A suggestion for further study is the investigation of Berlin Reservoir, which is immediately upstream from Lake Milton. Several sites with elevated concentrations of many elements were located in the southern part of Lake Milton, which is fed directly from Berlin Reservoir. It is a possibility that many of these contaminants may also be found in Berlin Reservoir. Another suggestion for further study is a more extensive sampling of the Lake Milton sites (the next time the lake is drained) in order to obtain better precision in the concentration values of the various areas. From such a study, better judgements can be made as to whether the elevated values of certain elements are due to pollution or contamination.

¹¹Hon, pp. 14-15.

¹²Hon, p. 137.

¹³Hon, p. 138.

¹⁴Hon, p. 100.

¹⁵Simons, E.N., Guide to Uncommon Metals, (Hart Pub. Company Inc., New York, 1967) p. 162.

BIBLIOGRAPHY

- ¹Butler, J. Jr., History of Youngstown and the Mahoning Valley Ohio. (American Historical Society, 1921), p.582.
- ²Butler, p.234.
- ³"Chronological history of Lake Milton dam," Youngstown Vindicator, Nov. 17, 1985, pp.A2-3.
- ⁴City Planning Commission, Recreation Development Plan for Lake Milton Reservoir. Report No. 62-6, (Youngstown Ohio, Dec. 1962), p.6.
- ⁵"Milton dwellers hope to reclaim paradise lost," Youngstown Vindicator, March 20, 1988, p.A-1.
- ⁶"City Park Commission acted to protect Lake Milton dam by ordering less water impounded behind it," Youngstown Vindicator, Aug. 7, 1972, pp.1-2.
- ⁷"Ungaro, State reach accord on lake transfer," Youngstown Vindicator, March 11, 1988, p.1.
- ⁸White, J.P.III, M.S. Thesis, Youngstown State University, August, 1985.
- ⁹Muntean, R.A., M.S. Thesis, Youngstown State University, June, 1974.
- ¹⁰Taylor, D., Neutron Irradiation and Activation Analysis. (D. Van Nostrand Inc., 1964), pp.31-32.
- ¹¹Rakovic, M., Activation Analysis. (Academia, Prague, 1970), p.6.
- ¹²White, p.81.
- ¹³Hem, J.D., Study and Interpretation of the Chemical Characteristics of Natural Water. (United States Geological Survey, water supply paper 2254, 1985, 3rd ed.), p.5.
- ¹⁴Hem, pp.34-35.
- ¹⁵Hem, p.137.
- ¹⁶Hem, p.138.
- ¹⁷Hem, p.100.
- ¹⁸Simons, E.N., Guide to Uncommon Metals. (Hart Pub. Company Inc., New York, 1967) p.162.

¹⁹Hem, p.135.

²⁰Simons, p.88.

²¹Hem, p.142.

²²Simons, p.33.

²³Hem, p.145.

²⁴Simons, pp.5-6.

²⁵Hem, p.76.

²⁶Hem, p.149.

²⁷Hem, pp.144-145.

²⁸Adams, R. and Murray, F., Minerals: Kill or Cure. (Larchmont Books, New York, 1974), pp.182-183.

²⁹Nadkarni, R.A. and Morrison, G.H., Anal. Chim. Acta, 1978, 99, 139-140.

³⁰Butler, pp.772-773.

³¹"General Motors Corp. to drill for natural gas and oil on city-owned property at Lake Milton," Youngstown Vindicator, Nov. 25, 1976, p.1.

³²"Park and Recreation Commission proposes gas drilling beneath Lake Milton," Youngstown Vindicator, May 17, 1984, p.13.

³³Harris, A.G., Geology Dept., Y.S.U., personal communication.

³⁴"Refer ruling on hazard of Milton tanks," Youngstown Vindicator, Nov. 14, 1972, pp.2-7.

³⁵"Lake Milton, replacing the public beach at Craig Beach, which will be closed this season because of inadequate restroom facilities," Youngstown Vindicator, May 27, 1969, p.1.

³⁶"Sanitary conditions in cottages at Milton being checked," Youngstown Vindicator, April 19, 1941, p.4.

³⁷"Fishermen at Berlin Reservoir and Lake Milton can now safely eat their catches," Youngstown Vindicator, Aug. 6, 1974, pp.1-3.