TRACE ELEMENT DETERMINATIONS
OF
SEDIMENT AND WATER FROM
SELECTED SITES OF THE
BLANCHARD RIVER

PRESENTED IN FULFILLMENT
OF THE REQUIREMENT OF
GEOLoGY 570

TO
DR. WAYNE PETTYJOHN

BY
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SPRING QUARTER
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ABSTRACT

The results of the water samples collected from the Blanchard River revealed a raw water supply that has concentrations far below the standards set by the USPHS for finished water sources. The sediments from the Blanchard River showed significant quantities of trace elements, particularly mercury and zinc. The highest concentrations of mercury were found in areas where intensive spraying had taken place. Lead seemed to accumulate in areas adjacent to heavily travelled roads. Geological contamination was also suspected as a prime contributor of copper, zinc, and lead. Although no definite answers were reached by this investigation, the results conspicuously pointed out the extremely varied and complicated behavior patterns of trace elements in the environment. The accumulation of the trace elements in the river sediments although not posing a health hazard at the present time, could possibly be released into the water through some change in the Blanchard River's many chemical equilibrium systems involving plants, organisms, dissolved oxygen, sunlight, pH, and hardness. The essence of studies such as this is to give health authorities essential information in establishing realistic limits of trace elements in our drinking water.
INTRODUCTION AND ACKNOWLEDGEMENTS

For centuries man has tended to regard water supplies as fixed. Various forms of pollution, however, are rendering increasing amounts of water useless. While our total usable water supplies are being diminished by pollution, a mushrooming human population and rapid agricultural and industrial expansion have accelerated drastically our water demands. In order to effectively combat this environmental problem, a functional early warning research program should be maintained to promote an awareness of the crisis for the policymakers and general public. Investigators should illuminate and define into layman's jargon the data concerning the parameters that adequately describe water quality so that legislatures can take appropriate measures to eradicate the degradation of our water sources. In other words, before one can cope with the malignancy, the nature of the problem must be sufficiently understood. Hopefully, therefore, the results of this limited investigation will be of some benefit to a future researcher striving for a more complete understanding of water quality.

At the suggestion of Dr. Wayne Pettyjohn, I undertook this investigation of trace element concentrations of sediment and water samples from selected sites of the Blanchard River in order to (1) suggest possible origins of any trace elements found, (2) relate the concentrations of any trace elements detected in terms of associated biological disorders, and (3) note whether or not any distribution pattern existed in detected trace element concentrations. The collection area (Fig. 1)
encompassed almost the entire length of the Blanchard River which flows northwest through the Ohio Counties of Hardin, Hancock, and Putnam. After the fieldwork was accomplished, atomic-absorption spectroscopy was employed to determine the trace ion concentrations of copper, lead, mercury, and zinc from each of the collected samples.

I wish particularly to thank Dr. Wayne Pettyjohn whose guidance and stimulating conversations proved to be invaluable, and to Mr. Tom Schultz for patiently instructing the writer in atomic-absorption techniques. Laboratory facilities were provided by the Department of Geology, Ohio State University.

BACKGROUND AND PREVIOUS WORK

Since its inception in 1955 atomic-absorption spectroscopy has undergone rapid development in the field of chemical analysis. Tangible evidence of the sweeping acceptance of this type of chemical analysis is offered by the amount of published work, which shows no sign of levelling off in either quantity or quality (Munoz, 1968). The high sensitivity of atomic-absorption methods has provided a suitable means of analysis for trace elements that normally are quite difficult to determine by conventional analytical procedures. Although state and federal agencies have used atomic-absorption techniques for the detection of trace elements in water for several years, the literature is relatively bare of any work pertaining to trace element determinations of river sediments. A noteworthy exception, however, is a study of trace element determinations in sediment and water samples from the
Maumee River drainage basin investigated by Tom Schultz, an Ohio State University graduate student. Mr. Schultz's study is of particular interest to me because several of his collecting sites were within one-hundred yards from where I collected my samples.

**GEOLOGY OF THE AREA**

Throughout its course the Blanchard River drains an area in which the bedrock is predominantly dolomites of Silurian age (Fig. 2). Though of marine origin, the dolomites of the Blanchard River drainage basin contain relatively few fossils in contrast to their highly crystalline nature. For the most part the dolomites are even-bedded, slightly porous, and show an overall buff color with a few exposures in Hardin County that have tinges of purple. The entire drainage basin is overlain by unstratified glacial drift that thickens to approximately 64 feet north of the river while the drift south of the river thins to about 26 feet. Structurally, the area of study has a slight northerly slope due to the dominance of the Cincinnati Arch.

**FIELD METHODS**

Sixteen samples from eight predetermined sites were collected from the Blanchard River, 22 January 1972. (The region of collection lies wholly within the Maumee River drainage basin). The sites selected were collected fairly representatively as to peripheral population densities. That is, four sites were located in rural areas and four sites were situated in urban areas. From each collection site one sediment sample and one water sample were gathered.
SILURIAN DOLOMITES
OF THE
BLANCHARD RIVER DRAINAGE BASIN

(Fig. 2)

<table>
<thead>
<tr>
<th>FACTS ABOUT THE BLANCHARD RIVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Slope ........ 9 ft./mile</td>
</tr>
<tr>
<td>Length ................. 91 miles</td>
</tr>
<tr>
<td>Drainage .............. 762 miles</td>
</tr>
<tr>
<td>Mean Jan. Discharge .... 291 cfs</td>
</tr>
<tr>
<td>Mean Annual Discharge ... 130 cfs</td>
</tr>
</tbody>
</table>

from depths ranging from two to five feet. Fortunately, the river was frozen over which made accessibility to the deeper parts much easier. A homemade device fashioned from a broom handle and coat-hanger wire worked very efficiently as a scoop in order to obtain the samples. A clean polyethylene bottle was clamped on the of the broom handle by means of the coat-hanger and then the entire device was lowered to the river bottom acting as a miniature dredge in securing the sediment samples. In obtaining the water samples, the device was lowered to approximately 2-3 feet below the water surface. Each sample was, of course, marked with the appropriate location of collection and type of sample.

LOCATIONS OF COLLECTION
SITES (Fig. 3)

Listed below are the locations of the eight collecting sites.

Site A: The intersection of Ohio Route 701 and the Blanchard River in Hardin County.

Site B: Along Ohio Route 568 at the intersection of the Blanchard River and the Outlet in Hancock County.

Site C: Inside the Findlay city limits where the U. H. Kiefaber Co. abuts the river at the end of Jefferson Avenue.

Site D: Inside the Findlay city limits where US Route 224 intersects the Blanchard River—the west side of the bridge.

Site E: Inside the Findlay city limits two-hundred yards west of the I-75 bridge on the south bank.

Site F: The intersection of the Blanchard River and Hancock County Road 128 along the north bank.
Site G: The intersection of Ohio Route 3, old US Route 224 and the Blanchard River in Gilboa, Putnam County.

Site H: The base of the old bridge remnants where South Perry Street ends at the Blanchard River in Ottawa, Putnam County.

SAMPLE PREPARATION

Due to the fact that determinations by atomic-absorption techniques require a liquid specimen, the need for extracting the ions (elements) from the sediment samples for subsequent release into solution was very evident. The extraction procedure used for preparing the sediment samples was borrowed from Schultz. Two extracting agents were employed, ammonium acetate and a solution of hydrochloric acid and sulfuric acid. The former's purpose was to extract those trace metal ions adherring to the outer surfaces of the sediment particles. In other words, ions readily available to the environment in a brief time-span were extracted by this agent. The latter extracting agent, however, broke down the lattice structure of the colloidal sediment and released not only ions adherring to the surfaces of the particles but also within the interstices of the crystal lattices. The ions released by this extracting agent therefore represent that quantity of trace metal ions from the sediment particles available to the environment after extensive periods of chemical reactivity. Obviously, the water samples required no further preparation since the ions were already present in solution. The specific preparation of each sediment sample was as follows:

1) The sample was stirred for three minutes. The resulting
The Area Under Study

Blanchard River Sub-Basin

A = Collection Site

Fig. 3
suspension was then poured into two petri dishes and two plastic test tubes. (The dry weight of the tubes and dishes having previously been determined). One test tube and petri dish are marked "X" and the other pair is labeled "Y".

2) The wet weight of the petri dishes and test tubes was recorded.

3) The petri dishes were placed in an oven overnight in order to evaporate the water.

4) The dried sediment and petri dish were weighed. (Step 4 minus step 3 yields the weight of the dried sediment). The weight of the dried sediment divided by the wet sediment weight with the resulting proportion multiplied by the contents of the test tube (with the corresponding label) gives the actual dry weight of sediment in each test tube.

5) 30 ml of ammonium acetate was added to the test tubes labeled "X". A 30 ml solution containing .05 mole of hydrochloric acid and .025 mole of sulphuric acid was added to the tube marked "Y".

6) Both "X" and "Y" test tubes were placed in a shaker for thirty minutes. Following the shaking process, the test tubes were placed in a centrifuge for fifteen minutes.

7) The liquid was decanted from both "X" and "Y" test tubes into separate 100 ml flasks labeled "X" and "Y", respectively.

8) Steps 6 and 7 were repeated again for both "X" and "Y" test tubes.
The solutions of "X" and "Y" were poured into separate plastic bottles and marked according to their location, element being determined, and the particular extractant used. The solutions were then ready for analysis by the atomic-absorption spectrophotometer.

**DETERMINATIONS**

The samples were analyzed for their trace element concentrations by a Perkin-Elmer Model 303 Atomic-Absorption Spectrophotometer. Determinations were made for four elements: copper, mercury, lead, and zinc. Below is a compendium of machine operating conditions used for each element.

<table>
<thead>
<tr>
<th>Date Run</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/21/72</td>
<td>.05</td>
<td>.5</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>3/22/72</td>
<td>.1</td>
<td>1.0</td>
<td>2.5</td>
<td>.1</td>
</tr>
<tr>
<td>3/23/72</td>
<td>.1</td>
<td>1.0</td>
<td>2.5</td>
<td>.05</td>
</tr>
<tr>
<td>3/24/72</td>
<td>.1</td>
<td>1.0</td>
<td>2.5</td>
<td>.05</td>
</tr>
</tbody>
</table>

- **Color of Air-Acetylene Flame:** PALE-BLUE
- **Concentrations of Standards (ppm)***: .05, .5, 2.5, 1.0, .1
- **Noise Suppression:** 30, 30, 5, 5
- **Speed:** 10, 10, 10, 10
- **Scale Expansion:** 10, 1, 10, 1
- **Slit:** 3, 3, 4, 3
- **Wavelength of Cathode Lamp:** 3274 nm, 2537 nm, 2833 nm, 2138 nm

*The standards were diluted to the particular concentration using a 1000 ppm stock solution and the appropriate blank for the specific sample. That is, for the water samples the blank was dimineralized*
water; for the "X" samples it was ammonium acetate; and for "Y" samples the blank was the acid solution of HCl and H₂SO₄.

An excellent treatment of operating instructions for the Perkin-Elmer Model 303 is discussed in "Instructions, Model 303 Atomic-Absorption Spectrophotometer", listed in the references.

RESULTS

The procedure used to calculate the ppm of solution and ppm of dry sediment is a lengthy and tedious job. However, these calculations were greatly simplified through the use of a computer. Basically, the computer is performing the following functions:

1) After being fed the peak heights of the standards and samples (the peak heights represent % absorption) and the weights of the dry sediment samples, the % absorption is logarithmically converted to absorbance.

2) It creates a theoretical calibration curve by plotting absorbance versus concentration for the standards. The absorbance of the samples are located and where the horizontal extension of the absorbance meets the linear working curve the corresponding concentration at that particular point on the curve is the concentration of the Sample. (See drawing below)
In other words, if the absorbance of the sample is located within the linear working range, the ppm may be calculated from the following formula:

$$\text{Sample (ppm)} = \frac{(\text{net sample absorbance})(\text{standard concentration})}{(\text{net standard absorbance})}$$

The results of the trace element concentrations for 8 water samples, 8 "X" sediment samples, and 8 "Y" sediment samples are compiled on the following pages.
### RESULTS OF WATER SAMPLES

Concentrations in solution (ppm)

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>TRACE</td>
<td>7.75</td>
</tr>
<tr>
<td>B</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>TRACE</td>
<td>7.87</td>
</tr>
<tr>
<td>C</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.003</td>
<td>7.80</td>
</tr>
<tr>
<td>D</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
<td>8.10</td>
</tr>
<tr>
<td>E</td>
<td>TRACE</td>
<td>0.000</td>
<td>0.000</td>
<td>0.018</td>
<td>7.95</td>
</tr>
<tr>
<td>F</td>
<td>0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.006</td>
<td>7.82</td>
</tr>
<tr>
<td>G</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>TRACE</td>
<td>7.97</td>
</tr>
<tr>
<td>H</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>TRACE</td>
<td>7.85</td>
</tr>
</tbody>
</table>

### RESULTS OF SEDIMENT SAMPLES EXTRACTED BY "X"

Concentrations in dry sediment (ppm)

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.203</td>
<td>14.999</td>
<td>0.907</td>
<td>0.394</td>
</tr>
<tr>
<td>B</td>
<td>TRACE</td>
<td>0.000</td>
<td>0.000</td>
<td>5.017</td>
</tr>
<tr>
<td>C</td>
<td>TRACE</td>
<td>6.711</td>
<td>0.000</td>
<td>0.636</td>
</tr>
<tr>
<td>D</td>
<td>0.079</td>
<td>0.000</td>
<td>3.360</td>
<td>1.867</td>
</tr>
<tr>
<td>E</td>
<td>1.264</td>
<td>0.000</td>
<td>0.000</td>
<td>2.419</td>
</tr>
<tr>
<td>F</td>
<td>0.048</td>
<td>35.585</td>
<td>12.670</td>
<td>11.910</td>
</tr>
<tr>
<td>G</td>
<td>0.982</td>
<td>9.745</td>
<td>5.735</td>
<td>10.445</td>
</tr>
<tr>
<td>H</td>
<td>0.145</td>
<td>0.000</td>
<td>0.000</td>
<td>0.940</td>
</tr>
</tbody>
</table>

Note: The sites are listed in descending order going downstream.
RESULTS OF SEDIMENT SAMPLES EXTRACTED BY "Y"

Concentrations in dry sediment (\text{\mu g})

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TRACE</td>
<td>19.878</td>
<td>0.962</td>
<td>0.511</td>
</tr>
<tr>
<td>B</td>
<td>TRACE</td>
<td>0.000</td>
<td>22.088</td>
<td>21.468</td>
</tr>
<tr>
<td>C</td>
<td>TRACE</td>
<td>0.000</td>
<td>0.000</td>
<td>0.635</td>
</tr>
<tr>
<td>D</td>
<td>TRACE</td>
<td>35.794</td>
<td>2.363</td>
<td>3.117</td>
</tr>
<tr>
<td>E</td>
<td>TRACE</td>
<td>75.981</td>
<td>3.121</td>
<td>2.825</td>
</tr>
<tr>
<td>F</td>
<td>TRACE</td>
<td>29.901</td>
<td>1.314</td>
<td>11.924</td>
</tr>
<tr>
<td>G</td>
<td>7.078</td>
<td>79.063</td>
<td>6.835</td>
<td>19.800</td>
</tr>
<tr>
<td>H</td>
<td>2.313</td>
<td>7.632</td>
<td>0.702</td>
<td>5.187</td>
</tr>
</tbody>
</table>

Note: The sites are listed in descending order going downstream.
Concentration of Trace Elements in H2O

Copper
Zinc
Lead
Mercury

Location - Downstream
Concentration of Trace Elements Extracted by X

Copper
Mercury
Lead
Zinc
Concentration of Trace Elements Extracted by Y

- Copper
- Zinc
- Lead
- Mercury

Profile Concentrations

Location - Downstream

0 4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 68 72 76 80

(Pm)
GENERAL DISCUSSION

The results of the water analyses reveal concentrations well within the finished drinking water standards as set by two federal health agencies (See table 1). Studies comparing raw river water with finished drinking water indicate that the concentration of trace elements occurs with the same frequency in both which is probably due to the fact that public water works do not check nor treat the raw water for trace elements (Kopp, 1970). Comparing the water results with the sediment figures discloses incredible differences in concentrations that immediately makes one speculate about the significance of the comparison. For example, no mercury was detected in any of the water samples while the sediment samples indicated concentrations of mercury as high as 79 ppm. Does this imply that the mercury (and likewise the other elements) is accumulating in the sediments rather than being transported downstream by the water? Although the water samples suggest that the river is devoid for the most part of trace elements, there is no evidence that refutes the possibility of trace elements in the sediment being released slowly over the years through changes in chemical equilibriums involving water pH, hardness, dissolved oxygen content, sunlight, plants, bacteria, and unsuspected chemical species. Therefore, a strong case for federal agencies to create standards for river sediments could be argued over the fact that it is far easier to prevent pollution than to correct for it after it has occurred.
Table 1

<table>
<thead>
<tr>
<th>Metal</th>
<th>Permissible (ppm)</th>
<th>Desirable (typ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COPPER</td>
<td>1.0</td>
<td>virtually absent</td>
</tr>
<tr>
<td>LEAD</td>
<td>0.05</td>
<td>absent</td>
</tr>
<tr>
<td>MERCURY</td>
<td>no standard</td>
<td>no standard</td>
</tr>
<tr>
<td>ZINC</td>
<td>5.0</td>
<td>virtually absent</td>
</tr>
</tbody>
</table>

*USPHS standards of 1962

The US Dept. of Health has set standards for mercury:
- Permissible: NONE
- Desirable: NONE

Table 2

Technological Sources of Trace Elements in the Blanchard River Drainage Basin

<table>
<thead>
<tr>
<th>Manufactured electrical goods:</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>TV tubes, radio and TV transitors</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Fabricated machinery

Chemicals:
- Phenolic moulding
- Compounds, pesticides, disinfectants, fungicides, agricultural sprays, polyethylene film

Rubber Tires

Printing

Smelting & Plating

tetraethyl gasoline

Hospitals: medicinals, disinfectants

Burning of coal

Plumbing fixtures in local systems
POSSIBLE SOURCES OF THE TRACE ELEMENTS

The proportions of Cu, Hg, Pb, and Zn in the sediment and water of the Blanchard River can be attributed to either industrial, agricultural, or geological sources. It is also possible that human wastes could have increased the concentrations of these trace elements. Munoz (1968) claims to have detected all four of the elements in urine and feces samples with concentrations ranging from traces to .07 ppm. Table 2 on the preceding page lists possible technological sources (industrial and agricultural) located within the drainage basin that very likely could have contributed trace elements to the sediment and water of the Blanchard River. Obviously, trying to pinpoint a particular technological source as the culprit is hardly relevant due to the limited number of samples taken. However, a few observations may shed some light as to the prime suspects. For example, the predominantly agricultural areas (sites A, F, G) have very high mercury concentrations (19.878, 29.901, and 79.063 ppm, respectively) which could presumably be linked to the abundance of agricultural sprays used in these areas. Site D, although not located in an agricultural area, had 35.794 ppm of mercury in the sediment. A plausible explanation for this high concentration at this site might be effluents discharging from a large medical complex located about 600 yards upstream. According to Grant (1971), hospitals may contribute significant amounts of mercury to the environment in solutions of mercuric chloride which are used in cleaning tissue samples in pathology laboratories. The
79.063 ppm of mercury found at site E (within the Findlay city limits) might conceivably be due to the proximity of spacious parks located along both banks of the river that could require large amounts of insecticides for protective purposes. Of course, there is always the possibility that a significant portion of the mercury in the sediments could be attributed to windblown mercury vapors produced by the burning of coal. Site G shows fairly high concentrations of all four elements and if one glances at table 2 the only row that contains all the elements is the one containing pesticides, etc., thereby implying that agricultural sprays are the sources of the four elements at site G.

Lead seemed to occur in more significant quantities when the sampling sites were in juxtaposition to heavily traveled roads. Many workers claim that the use of tetraethyl lead in gasoline can give rise to critical levels of lead in nearby streams and soils (Warren, 1970). Site B with 22.088 ppm of lead was located within 30 yards of a major state route, but site E located just 200 yards west of an I75 bridge only recorded a concentration of 3.121 ppm. For some unexplainable reason the concentration of lead at the latter site is substantially reduced in contrast to the former site even though the volume of traffic on the I75 bridge is in all probability several times greater than the state route adjacent to site B. It is highly feasible that the results for lead are recording quantities introduced into the Blanchard River by the corrosive action of water on lead plumbing fixtures. Normally, however, lead pipes acquire
an internal protective coating that prevents this corrosive action, but if the pH and hardness are low, and the dissolved oxygen content high, this corrosive action would continue to release lead ions into the local water supplies.

If the local bedrock had any trace elements incorporated into the sediment at the time of formation, weathering of the bedrock should allow for at least small percentages of the trace elements to reach the Blanchard River. According to Birsa (1972), the dolomites of this region have concentrations of Cu ranging from 11.4 to 7.05 ppm and concentrations of Pb varying from 42.4 to 27.1 ppm. Every sediment sample tested for copper recorded at least a trace while seven of eight sites tested for lead in the sediment had concentrations greater than 0.7 ppm (using the figures for the samples extracted by "Y"). The portion of trace elements contributed by the local bedrock to the Blanchard River would be very difficult indeed to discern. A few researchers, however, suspect that geological pollution (weathering of the bedrock) is quantitatively by far the greatest contributor to abnormal contents of copper, zinc, and lead in soils. The soil or weathered bedrock is then subject to overland wash which presumably could deliver a significant amount of trace elements to the Blanchard River. Warren (1970) says that soils frequently contain, in terms of extractable trace elements, somewhere in the range of 5-70 ppm of copper, 35-300 ppm of zinc, and from 2-10 ppm of lead. These figures correspond nicely with those of Birsa's figures cited previously. Therefore,
it may be very likely that the local bedrock contains a significant concentration of zinc that might be reflected in the sediment and water analyses. Unfortunately though, Birsa never examined the dolomites for zinc.

DISTRIBUTION PATTERNS

The only apparent distribution pattern seems to be that mercury is concentrated where agricultural sprays are frequently used. However, the results seem to indicate that trace elements do not accumulate in greater proportions farther downstream, but rather tend to localize, conceivably around the region where they first entered the water.

PHYSIOLOGICAL SIGNIFICANCE OF TRACE ELEMENTS IN THE BLANCHARD RIVER

The physiological significance of each trace element found in the sediment and water samples of the Blanchard River should be assessed in terms of long-term exposures to even the smallest doses of a trace element.

Toxicity, the inherent property of a substance that injures growth or metabolism when it is concentrated above a certain limit, although not generally associated with copper, can be imparted to individuals who receive large prolonged doses. Individuals orally consuming doses of 60-80 mg for prolonged periods may suffer severe liver damage. Man has a built-in mechanism towards toxic levels of copper in water, for excessive copper imparts an undesirable taste to drinking water when levels exceed 2 ppm. However, depending on the individual's taste perception, the detectable limit of copper may vary from 2-5 ppm. Copper is essential to human metabolism and
a deficiency of copper in infants results in nutrional anemia. The average adult requires 3 mg daily while a child requires only 2 mg. Most of the copper ingested by the body is excreted rather than being retained. Victims of Wilson's disease, however, have not inherited the mechanism to excrete excessive dosages of copper. The element accumulates first in the liver and then in the brain and by time adolescence arrives death occurs. Another inherited disease, hemochromatosis, a disorder of iron metabolism, results from excessive levels of copper. It is characterized by hepatic cirrhosis, excess deposition of iron in tissues, and decreased carbohydrate tolerance. It is a rare individual who suffers from copper deficiency, which is fortunate since copper participates in so many vital body functions. Probably its most critical function is its interaction with iron in blood formation. Copper is also found in a number of protein compounds, especially those functioning as enzymes with an oxidase function. The activities of these enzymes are dependent upon their copper content. Copper is also essential for hair pigmentation and for the normal development of vascular connective tissue.

Zinc is another trace element that is more beneficial to mankind than deleterious. In fact, the only cases of reported zinc poisoning occurred when individuals consumed acidic food cooked in galvanized iron vessels. Generally speaking, it is far more common for men to have zinc deficiency. Individuals deficient in zinc are prevalent in hospital populations and persons having metabolic diseases. The very young, the very old, and the very poor are also
very prone to experience a zinc deficiency. The average adult intake of zinc varies from 10-15 mg/day, but men could probably consume ten times this amount before showing any signs of zinc poisoning. Although the USPHS has established that 5 ppm of zinc in drinking water as a recommended level, they have not as yet determined a maximum level. A high concentration of zinc in the body induces copper deficiency, probably by displacing the copper. Once the excess zinc upsets the copper levels, complications develop such as a breakdown in the formation of blood cells and some copper dependent enzymes becoming non-functional. Clinically, zinc deficiency can be detected by a loss of taste. Unfortunately though, most effects of zinc deficiency are more damaging such as the inclusion of cadmium and radioactive zinc-65 in the enzyme bonding sites normally occupied by ordinary zinc. Zinc has been shown to greatly improve the rate and process of wound healing and also of bone and arterial repair. Zinc therapy has had beneficial effects upon atherosclerosis by allowing increased volumes of blood to reach areas that were previously suffering from insufficient blood quantities due to damaged vessels. Zinc is also a critical constituent of metalloenzymes associated with protein synthesis.

Due to man's brief evolutionary exposure to lead, this trace element is one of the most dangerous substances found in the environment today. Man has had contact with lead for only the most recent 5000 years of his existence, and therefore has not yet developed a homeostatic mechanism for it. Lead taken into the body in quantities in excess of certain "low limits" is a cumulative poison. Prolonged
exposure to even small doses could cause a serious illness or even death. With so many possible sources of lead contamination, and the modes of entry into the body so diverse (food, water, air), it is essential that health agencies maintain a very low standard for lead in the water supplies. The USPHS has established .05 ppm as the maximum level in drinking water. Therefore, the total amount of lead taken into the body by breathing, drinking, and eating (minus small amounts excreted by the body) determines whether or not this cumulative substance is poisoning the individual. Mild symptoms of lead poisoning are lethargy, constipation, and moroseness. As the poisoning becomes more severe insomnia, nausea, and anemia occur. The severest cases are characterized usually by convulsive attacks or coma with death very imminent. The daily consumption of lead in amounts as low as 0.1 mg over several years could be fatal.

At one time, industrial discharge of inorganic mercury did not appear to pose much of a health problem, since inorganic mercury is readily excreted by the body and absorbed in large amounts (Wood, 1971). Since, then, it has been discovered that a reaction catalyzed by microorganisms capable of synthesizing vitamin B₁₂, converts inorganic mercury to methyl mercury, the most lethal organic mercury compound. Thus, if large amounts of inorganic mercury are in the river sediments, microorganisms can convert the less biologically harmful form to the highly toxic organic complex at the expense of our environment by releasing the methyl mercury into the water. It is a likely possibility, therefore, that the large accumulations of mercury in the Blanchard River sediment could be converted to methyl mercury at some later time more conducive for the reaction to take place. The route for
the synthesis of methyl mercury is illustrated in Fig. 4. The extent of pollution through agricultural use of methyl mercury compounds is not known precisely since the compounds can be disseminated in the environment several ways. These organic agricultural compounds are still in widespread use throughout Ohio and the rest of the country. Organic mercury compounds are cumulative poisons that cause neurological disorders and eventual death. Although there are no USPHS standards regulating mercury, adults may drink safely water containing 4-12 mg daily. Fatal doses of mercury in water range from 75-300 mg/day.

SUMMARY AND CONCLUSIONS

The results of the water samples from the Blanchard River revealed a raw water supply that was almost devoid of trace elements except for slight amounts of copper and zinc. The sediments samples showed significant quantities of trace elements that in some instances seemed to reflect close proximity to a possible source. For example, mercury appeared to accumulate in the sediment near areas where intensive spraying had been done. Lead seemed to accumulate in areas where heavily traveled highways were within a short distance of the collection sites (although an anomalous result was noted at a site located close to a major expressway). Although the river water is free for the most part of trace elements, the high concentrations of trace elements in the river sediment could be released into the river water possibly by some changes in the dynamic chemical equilibrium systems of the river. The various
physiological disorders that could arise if toxic concentrations of the trace elements were in the finished drinking water emphasizes the urgent need for more stringent penalties against polluters. Man, however, is not always the sole polluter. Geological contamination from the local bedrock may possibly be a prime contributor of copper, lead, and zinc found in the Blanchard River sediments.

Before any conclusive answers can be drawn as to the sources of the trace elements, more sophisticated and considerably larger investigations are needed to study the bedrock, soils, plants, river water, river sediments, microorganisms in the river water, and the various chemical equilibriums of the river water in order to better acquaint ourselves with the behavior patterns of trace elements in the environment. All of this proposed research would be of the utmost practical value for it would provide health officials with essential information in establishing realistic limits or tolerable concentrations of the various trace elements in drinking water (Kopp, 1969).
SELECTED REFERENCES


