



The Environmental Mercury Problem

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DEDICATION

This book is dedicated to the Michigan House of Representatives Great Lakes Contamination (MERCURY) Committee resulting from House Resolution 424 and under the chairmanship of Joseph M. Snyder, Representative for Michigan District 74.

Representative Snyder's concern for the environment contributed greatly to the implementation of this project, and I would like to acknowledge my gratitude for his personal encouragement.

Frank M. D'Itri

THE AUTHOR

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Dr. D'Itri received his B.S. degree in Zoology in 1955 and his M.S. and Ph.D. degrees in Analytical Chemistry in 1966 and 1968, respectively, all from Michigan State. Dr. D'Itri was a National Institute of Health Summer Fellow, 1964-67, and a Socony-Mobil Fellow at Michigan State, 1967-68. He is a member of the American Chemical Society, Sigma Xi, and Michigan Academy of Science, Arts and Letters.

He has written many papers pertaining to his major research interest, the analytical aspects of water and sediment chemistry with special interest on the transformation and translocation of mercury.

TABLE OF CONTENTS

Introduction	1
Recommendations to Subcommittee	3
Chapter I History and Historical Uses of Mercury	5
Chapter II Background Concentrations of Mercury in the Environment	9
Chapter III Uses and Sources of Mercury Contamination in the Environment	17
Chapter IV Analytical Methods for the Determination of Mercury	33
Chapter V Translocation of Mercury in Plants and Movement Through the Food Chain	51
Chapter VI Biological Methylation of Mercury in the Environment	63
Chapter VII The Decontamination and Restoration of Mercury Polluted Areas	69
Chapter VIII Epidemiology and Toxicology of Mercury	73
Chapter IX Chronology of the World's Mercury Poisoning Problem	87
Conversion Units for Mercury	107
References	108

INTRODUCTION

Following reports of the calamitous introduction of mercury into the environment, House Resolution Number 424 was introduced in the Michigan House of Representatives during the 75th Legislative session in 1970. The text of this Resolution is reproduced hereto.

No. 48
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HOUSE OF REPRESENTATIVES
75th Legislature
Regular Session of 1970

Lansing, Wednesday, April 8, 1970.

Reps. Snyder, Copeland, Goemaere, Kehres, Sackett, and Holmes offered the following resolution:

House Resolution No. 424.

A resolution creating a special committee to evaluate the scope and effectiveness of regulations relative to contamination problems of the Great Lakes.

Whereas, Recent reports relative to mercury poisoning contamination in Lake St. Clair and the possibility of further poisoning in the Great Lakes poses a continuing serious problem which must be met head-on; and

Whereas, Due to the geographical location of the Great Lakes, with Michigan being the recipient of the benefits of the Great Lakes as well as pollution effects thereof, it is essential that the State of Michigan work with and cooperate with various states and foreign countries relative to seeking solutions to the Great Lakes pollution problems; now therefore be it

Resolved by the House of Representatives, That there is created a special committee of the House to consist of five members to be appointed by the Speaker to function now and during the interim between the 1970 and 1971 regular sessions of the Legislature to study and evaluate the scope and effectiveness of Great Lakes contamination testing programs; to look into the damaging delays in closing down facilities which cause contamination problems once they are known to exist; and to look into existing plans for the immediate and long-range preparations for the protection and preservation of the Great Lakes and examine the degree and effectiveness of international, federal and state cooperation relative to the pollution and contamination of the Great Lakes; and to report its findings and recommendations to the 1971 Legislature; and be it further

Resolved, That the committee may subpoena witnesses, administer oaths and examine the books and records of any person, partnership, association or corporation, public or private, involved in a matter properly before the committee; and be it further

Resolved, That the committee may employ such consultants, aides and assistants as it deems necessary to conduct its study; the committee may call upon the Legislative Service Bureau, subject to approval of the Legislative Council, for such services and assistance as it deems necessary and may request information and assistance from state departments and agencies; and be it further

Resolved, That the members of the committee shall serve without compensation, but shall be entitled to actual and necessary travel and other expenses incurred in the performance of official duties, to be paid from the appropriation to the House of Representatives.

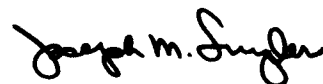
Passed by House on April 30, 1970, Rep. Snyder appointed Chairman.

In view of the conflicting opinions that were prevalent when the effects of mercury on the environment were noted, the House of Representatives Committee that introduced Bill Number 424 enlisted the assistance of Dr. Howard Tanner, Director of the Department of Natural Resources at Michigan State University. Dr. Tanner recommended the assistance of Dr. Frank M. D'Itri, Assistant Professor of Water Chemistry at Michigan State University; and Dr. D'Itri directed the project that resulted in this report.

It is our opinion that this report is the most comprehensive and detailed study that has been made of this subject, and we are deeply grateful for the professional assistance received from both Dr. Tanner and Dr. D'Itri. Their effort was voluntary and without compensation.

House Resolution Number 45 has reactivated the committee that sponsored this research for another year. In 1971 the committee intends to introduce the legislation recommended in this report and to hold public hearings in the areas involved to determine the scope of the problem and to recommend both short term and long range remedies.

Sincerely,



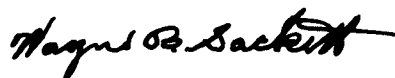
Joseph M. Snyder, Chairman



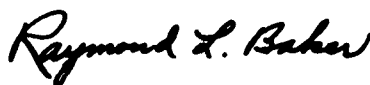
Raymond C. Kehres



Warren N. Goemaere



Wayne B. Sackett



Raymond L. Baker

Michigan House of Representatives
May 25, 1971

RECOMMENDATIONS TO THE SUBCOMMITTEE

The urgent need to eliminate or very sharply curtail the discharge of mercury into the environment is paramount to the health and well being of the American people. That all forms of mercury are hazardous is widely recognized, but what is more devastating to our society is that all forms of mercury appear to have the potential to be converted into highly toxic mono- or dimethylmercury. Therefore, several methods of dealing with the mercury contamination problem have been suggested. The following are recommended changes in current regulations and law enforcement to help prevent environmental contamination problems of this type in the future.

1. Ban the use and sale of all alkylmercury-containing compounds into the Michigan environment. They are simply too toxic to be used safely.

2. Establish a complete inventory of mercury uses and their respective amounts of discharge. The use of mercury-containing pesticides should also be severely restricted and they should be used only when there is a demonstrated and urgent need for the compound.

3. Require that all manufacturers, especially in the chlor-alkali industry, reduce their discharges of mercury into the total environment — air, water, and land — at least to the background levels of that area. The background levels may be difficult to assess, but they could be determined approximately through the average mercury content of unpolluted parts of the state.

4. Register all users of more than one pound of any form of mercury with the State of Michigan and require them to provide a yearly accounting of their mercury inventory wherein all losses should be identified.

5. Require all large users of fossil fuels except individual home owners in Michigan to determine the amounts of mercury present in the coal or crude oil before it is burned or converted into another product. Furthermore, determining the mercury content should be required as part of ash analyses.

6. Require that all compounds or products which contain mercury state this information on the product or package; and the citizenry should be requested not to incinerate these products. Furthermore, the state could set up collection depots where people could dispose of mercury-containing products. These collection depots could be local fire stations. Ideally, a provision could be made to recover and recycle the mercury or to dispose of mercury containing refuse by controlled procedures in a safe area. And all manufacturers and farmers should be encouraged to use nonmercurial fungicides and pesticides.

7. Reinstate the catch and release rule for all fish caught in the St. Clair River and Lake St. Clair until the mercury levels decrease significantly in fish taken from this area. The authority for this action is vested in the Michigan Department of Health.

That such action is necessary was expressed in the Michigan Department of Agriculture publication "Accumulative Report on the Analysis for Mercury in Great Lakes Fish" of April 28, 1971. Of the 73 fish tested from Lake St. Clair, the total mercury levels ranged from undetectable to 6.65 ppm. And significantly, 59% contained mercury levels in excess of the 0.5 ppm guideline recommended by the Federal Drug Administration. Moreover, the overall average mercury concentration in all 73 fish was 0.97 ppm which is the level at which the FDA removed swordfish from the market as an immediate health hazard.

The mercury levels in the Lake St. Clair fish are less than those of the seafood that caused the Minamata, Japan epidemic. Clearly, however, no persons have been reported

to have symptoms of methylmercury intoxication in Michigan because Americans do not normally consume large amounts of fish, not because a clear and present danger does not exist. Rather, Dr. Roger C. Herdman of the New York State Health Department recently reported that a woman who consumed 10 oz of swordfish per day (or 4.4 lb per week) for nine months was stricken with methylmercury poisoning. Furthermore, during his recent visit to Michigan for an international mercury pollution conference, Professor Tadeo Takeuchi of Kumamoto University, Japan (the scientist who discovered that organic mercury was the cause of Minamata Disease) recommended that fish taken from Lake St. Clair not be eaten, especially by pregnant women. Professor Takeuchi cautioned that a maximum of *one meal* of fish taken from Lake St. Clair be consumed every seven to fourteen days. Unless public consciousness of this mercury threat is maintained at a high level for a long time, an impossible task, such limited utilization of fish is likely to be regarded as undue governmental restraint. Consequently, if some fish are permitted to be consumed, the danger will remain, and the gradual buildup of mercury in human tissues will continue. And, of course, the threat is greatest to the unborn child; and the woman who is not aware of her pregnancy yet can jeopardize a life unintentionally. But the major consideration is that although the discharge of mercury into the lake is stopped, studies have shown that the pollution problem remains for a number of years. For a long time, then, even occasional mercury consumption could result in a buildup of this hazardous chemical in the human body.

HISTORY AND HISTORICAL USES OF MERCURY

Summary

Mercury and its ore, cinnabar, have been known and used since prehistoric times. However, the uses of mercury and cinnabar were limited primarily to medicines, pure and applied chemistry, amalgamation, and various decorations until approximately 1900.

The production of over 90% of the world's annual supply of approximately 20 million pounds of mercury comes from only seven countries in the world. Mercury is normally refined by roasting the cinnabar ore which causes the mercury to be vaporized and subsequently condensed and recovered.

Mercury and its principal ore, cinnabar, have been known since prehistoric times; and their respective discoveries are lost in the unrecorded history of antiquity. The ancient Hindus and Chinese were familiar with the ore and its metal,¹ but reliable data are lacking about the first written record of its use because histories written by the ancient Hindu and Chinese authorities have frequently been revised and addenda have been appended. However, it appears reasonable that mercury and cinnabar were first mined more than 2,300 years ago. Moreover, samples of mercury were reported to have been found in ancient Egyptian tombs that date to 1500 or 1600 B.C.² But Aristotle (384-322 B.C.) is credited with the first recorded mention of mercury in connection with a religious ceremony. More than a century later, the Chinese constructed a relief map of China that depicted the oceans and rivers as liquid Quicksilver.

From the limited historical data that are available, ancient civilizations apparently valued cinnabar, the mercury ore, highly because of its density and reddish-gold color. Therefore, it appears probable that the first practical use of cinnabar was because of its color. After the Punic Wars large amounts of cinnabar-containing ore were transported to Rome where the ore was reduced to the highly prized pigment vermilion which was used to decorate Roman villas and make rouges and other beauty products.³ This use of vermilion as a high grade paint pigment has survived into the 20th century.

By the first century B.C., mercury was a relatively familiar substance. Prepared by roasting the mercury-bearing ore in air, this process to distill off the metallic mercury was well-known.

The first evidence of mercury technology other than its mining and smelting procedures or use as decoration can also be traced back to this era. Vitruvius, the famous Roman architect, described the process of amalgamation, probably the first practical nondecorative use of mercury. He noted that mercury readily dissolved gold, and he described a method for recovering gold that had been woven into a garment.⁴ One hundred years later, in describing the same process, Pliny wrote that 10,000 lb of mercury were brought to Rome from Spain each year, and he described an improvement in its use to recover gold.

From these early times, mercury has become increasingly important as new uses were discovered. From the time of Aristotle through the Middle Ages, accounts record the prominence of mercury and mercury salts in the annals of medicine. The early Chinese believed cinnabar and mercury were medicines that prolong life, and several emperors were reputed to have died through the ingestion of mercury or cinnabar in futile attempts to secure immortality.⁵ The ancient Hindus, on the other hand, thought of mercury as an aphrodisiac. And as early as the first century A.D., Dioscorides Pedanus, a Greek physician, and Pliny the Elder used mercury in a medicinal ointment. Moreover, Rhazes, Mesue, Avicenna, and Arnold of Villanova all recommended bichloride of mercury and mercury containing ointments or salves to treat various skin diseases. Paracelsus probably introduced the most unusual medicinal use for mercury. He digested mercury with oil of vitriol (sulfuric acid) and distilled it with Spiritus vini (alcohol) as a cure for syphilis.²

While mercury and mercury-containing com-

pounds appear to be completely ineffective in the treatment and cure of syphilis, this use of mercury persisted as late as the 1930's partly because of Paracelsus' great reputation. For example, in 1927 a drug designed to treat syphilis and leprosy simultaneously consisted of a mercury derivative that was rendered soluble in one of the complex compounds of chaulmoogra oil.⁶

Despite such varied and longstanding medicinal uses, the toxic nature of mercury was reported by a number of ancient authors including Hippocrates, Pliny, Galen, and Avicenna.⁷ In 1493 Ulrich Ellenborg was the first to demonstrate adequately the dangers of mercury vapor.⁸ In 1533 Paracelsus wrote a book about occupational diseases in which he described in detail the mercury poisoning of miners.⁸ Although Paracelsus was intrigued with mercury, he considered it an important metal that was deficient in its coagulation capability, which he considered to be the end product of all metals. Paracelsus believed that all metals were liquid mercury up to the midpoint of the coagulation process. Therefore, he thought gold was simply mercury which had lost its mercurial nature by coagulation. Consequently, he expended much unsuccessful effort trying to coagulate mercury sufficiently to convert it into gold.⁹

To the end of the Middle Ages, the exact chemical and physical nature of mercury remained unknown and seemingly paradoxical. Many early investigators, including the alchemists, were fascinated with such a unique and mysterious material as this liquid metal, and it played an important role as an intermediate in efforts to transmute selected base metals into gold.¹⁰

As late as the middle of the 18th century, mercury was not universally classified among the metals because of its liquid nature. This concept was disproved in St. Petersburg, Russia during the intensely cold winter of 1759-1760 when the mercury in a thermometer became solid during an experiment performed by Braun and Lomonosov. They established the freezing point of mercury at about -40°F.¹¹

During the 17th and 18th centuries as chemistry slowly evolved from alchemy into a more exact science, the physical and chemical properties of mercury were either discovered or reappraised. The modern chemical symbol for mercury, Hg, was derived from its Latin name *Hydrargyrum*, meaning liquid-silver. This name

reflects its appearance and its ability to impart a silvery color to other metals. Occasionally mercury is also referred to as quicksilver, a derivative from the Latin translation of *argentum Vivum*, meaning live or quick silver.

And we now know elemental mercury is unique because it is the only metal which is a liquid at room temperature. However, this characteristic is not singular on hot days since both metallic cesium and gallium become liquid at 83.3 and 85.6°F, respectively. Another characteristic of mercury is that it is a very dense liquid that weighs about 13.6 times as much as the same unit volume of water. This physical property of mercury led Torricelli to discover the barometer around the year 1644. And the fact that mercury remains a liquid over a wide temperature range (freezing point -38.9°C, -37.9°F; boiling point 356.6°C, 673.9°F), coupled with its almost constant thermal coefficient of expansion over a temperature range from 0° to about 300°C, accounts for its wide use in thermometers. Another physical property of mercury that was known in antiquity is its ability to dissolve all the common metals except iron and platinum to form alloys. These alloys, called amalgams, may be solid or liquid. Probably the most distinctive property of mercury amalgams is that the chemical reactivity of the metal dissolved in mercury is lowered. This property is exploited in the chlor-alkali industry which utilizes the mercury cell method to produce chlorine and caustic soda. Mercury metal is a poor conductor of heat compared with other common metals, but it is a moderately good conductor of electricity, explaining its wide use in the electrical and control instruments industries.

With respect to the environmental mercury contamination problem, probably the most important physical property of mercury is its volatility. Because of its relatively high vapor pressure, mercury is easily evaporated into the atmosphere. Thus, its translocation into the environment is assured. If mercury is allowed to evaporate in closed rooms, dangerous levels of mercury are readily attained in the air. For example, air saturated with mercury vapor at 20°C (68°F) exceeds the maximum allowable concentration of 0.1 mg/m³ of air by more than 130-fold.

Mercury and cinnabar deposits usually occur in geologically young volcanic areas, particularly those with tectonic movement where hot springs

in fractive zones may sometimes contain mercury as readily soluble double sulfides. Cinnabar, metacinnabarite, and calomel are three of the limited number of important mercury-containing minerals. However, small amounts of native mercury can be found in some mineral deposits. The most important mercury ore, cinnabar or HgS , occurs as the predominant sulfide mineral in most mercury deposits and is generally formed under low pressure hydrothermal conditions. Therefore, cinnabar is commonly associated with minerals such as pyrite, marcasite, chalcedony, quartz, calcite, dolomite, and ankerite; or it forms as a result of hot spring activity.

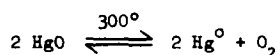
The most important cinnabar deposit in the world is at Almaden, Ciudad Real, Spain, where it occurs as an impregnation and replacement of the quartzite when mercury minerals are deposited in a porous sandstone from a hot thermal solution. While the normal mercury content in ore ranges from 0.3 to 8% in many places, in the San Pedro vein on the slopes of the Sierra Morena mountains where the Almaden mine is located, the ore has averaged 20% mercury.¹²

Since the Phoenicians first began mining operations in about 700 B.C., the Almaden district has produced in excess of 500 million lb of mercury. The Almaden mine together with only three other districts in the world — Idria in Yugoslavia, Monte Amiata in Italy, and the central coastal area of California — has dominated the world's mercury production. While mercury deposits are known throughout the world, in 1968, as in previous years, over 90% of the world's mercury supply of over 19 million lb came from the following seven sources:¹³ Spain, 22.4%; Italy, 20.4%; USSR, 17.6%; U.S.A., 11.3%; China, 7.8%; Yugoslavia, 6.1%; Mexico, 5.2%; and all other countries, 9.1%.

The most important deposits in the U.S. are in the California coastal mountain range from Del Norte County to San Diego County. The largest American producers of mercury are the New Almaden and New Idria mines that are located in Santa Clara and San Benito Counties. Mercury also occurs with gold and stibnite near National, Nevada, in Utah, Oregon, near Terlingua, Texas,

and in Pike County, Arkansas. In addition, during 1968, mercury was mined in Alaska, Arizona, Idaho, Oregon, and Washington, with California and Nevada accounting for approximately 90% of the total domestic production.¹⁴ More complete descriptions of the most important mercury deposits in the U.S. and in the world have been compiled by Lamey,¹⁵ White,¹⁶ and Jonasson and Boyle.¹⁷

Generally, the mercury ore is mined from underground deposits. However, a small percentage of the ore is removed by open-pit, surface mining techniques. After the ore is mined, the most common process for recovering the metal is to roast the crushed ore at 500 to 600°C in the presence of air. Under these conditions the mercury sulfide decomposes, and the sulfur can be removed as sulfur dioxide or ferrous sulfide while the mercury is being volatilized by heat. Then the mercury vapors are condensed into a liquid in a series of water-cooled condensers. The liquid mercury is then drained into collecting tanks. An alternate way of preparing mercury is to dissolve the ore in an alkaline sodium sulfide solution. The mercury is then precipitated out by adding aluminum turnings and purified by distillation. The usual metal recovery from sulfidic minerals involves roasting to the oxides and thermal reduction with carbon. The addition of carbon is unnecessary to recover the mercury because any intermediate mercury oxide decomposes directly to the metal at elevated temperatures; mercuric oxide is thermally unstable and decomposes according to the following equation:



The product of the roasting process is prime virgin mercury metal which is usually at least 99.9% pure and is acceptable for most industrial uses without further purification.¹⁸ This mercury is sold in flasks, each of which contains 76 lb of the metal. The average price of mercury per 76-lb flask has increased from less than \$50 in 1922 to \$700 in 1965.¹⁹ The market price as of April 23, 1971 was \$310 per 76-lb flask.²⁰

BACKGROUND CONCENTRATIONS OF MERCURY IN THE ENVIRONMENT

Summary

The background concentration of mercury in the environment is difficult to determine because of its ubiquitous nature and its many contamination sources. In soils a reasonable background mercury concentration would be between 10 and 150 ppb. However, higher mercury levels are associated with soil containing high humus or organic fractions. Depending on the extent of urbanization, background atmospheric mercury concentrations varying between 0.001 and 50 ng/m³ are common. Rainwater has been reported to contain a concentration of 0.33 ppb.

The lakes, rivers, and oceans of the world are the key method of transport for mercury in the environment. The normal background levels of mercury in these waters are in the range of 0.02 to 0.7 ppb, but they are generally less than 0.1 ppb. Furthermore, it must be concluded that in many areas human activity has raised the mercury content of the environment far above natural levels.

In nature, mercury is found in a number of forms. Cinnabar (HgS) and its polymorph meta-cinnabar (HgS) are the most important primary minerals containing mercury. Additionally, Livingstonite (HgSb₄S₇) and some mercury-containing sulfur salts such as tetrahedrite have also become important ore sources.^{1,7} The mercury content of some common ore and gangue minerals is given in Table 1.

Background concentrations of mercury in nature that have not been contaminated by man are difficult to determine. Wide and anomalous variations in the mercury background concentrations exist for a variety of reasons (Figure 1). For example, since mercury is mobile in high temperature environments, igneous rocks should contain less mercury than sedimentary formations such as shale, but these values are highly variable (see Tables 2-4). And because of the volatile nature of mercury, dissemination aureoles form around cinnabar deposits. These aureoles can be quite extensive and serve as pathfinders in searching for mercury or any sulfide metals associated with mercury deposits.²¹⁻²³ Fredrick and Hawkes²⁴ reported that the soils underlying extensive systems of mineral rich ore veins in the Pachuca-Real Del Monte District of Mexico contained from 250 to 1,900 ppb of mercury over a background value of 50 ppb. Another factor that makes it difficult to ascertain the background mercury concentrations is that some areas con-

taining mercury mineralizations have been polluted with mercury. And the amount of mercury from pollution cannot be separated from the mercury background concentration levels which have been reported in the literature as ranging from one to over 500 ppb.²⁴⁻³⁴ For example, Martin³³ reported the natural background levels of some English soils to fall between the values of 10 and 60 ppb, whereas Andersson³⁴ reported that the mercury content of 200 soil samples ranged between 20 and 920 ppb, with an average of 70 ppb. Kimura and Miller³⁵ found the natural mercury content of sandy loam soil from Puyallup, Washington, U.S.A., to be 166 ppb.

Reports of what appear to be inordinately high mercury soil concentrations such as Andersson's 920 ppb are especially significant in areas which are devoid of mercury mineralizations. While the mercury content of a given sample will vary in different geographical locations, varying amounts of humic materials and clays in the soil fractions modify the soils' ability to accumulate mercury^{2,7} (see Table 5). Andersson^{29,34} reported that the humus or organic fraction of a soil has the greatest affinity for mercury, and a direct relationship exists between these two parameters. Andersson found that the mercury content of the organic component of a moraine soil was 1,100 ppb, while its mineral component contained only 80 ppb of mercury.³⁴ Furthermore, from these studies it appears that the adsorption-desorption of mercury