Trace Metals in Michigan's Ecosystems

Prepared By

Trace Metals Relative Risk Task Force
Elwin Evans, Ph.D., Chair
April 1998

Michigan Department of Environmental Quality
Office of Special Environmental Projects
http://www.deq.state.mi.us

John Engler, Governor
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Trace Metal Relative Risk Task Force

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EXECUTIVE SUMMARY

The Governor's Relative Risk Program was initiated in September 1991 with the creation of three multi-disciplined committees composed of scientists, citizens, and representatives of governmental agencies, respectively. The purpose of each committee was to identify and evaluate known and suspected environmental problems, decide which problems were of particular concern, and assign a relative rank to each by comparing the risks it posed to the environment and quality of life. The resulting report, entitled, *Michigan's Environment and Relative Risk* was presented to the Governor in July 1992.

The report identified 24 risk issues and ranked each in terms of concern as “high-high”, “high”, “medium-high”, or “medium”. Trace elements in the ecosystem were ranked as having a “high” risk because of their toxic nature and the limited knowledge of their distribution, concentration, trends, sources, fate and biological impacts.

Toxic trace elements are only one class of substances that have been widely dispersed in the environment due to human activities. Limited data for the Great Lakes region suggest that concentrations of most of these toxic substances have declined over the past 25 years due to regulations and conservation.

Michigan currently does not have a comprehensive program to monitor toxic trace elements in a systematic and scientifically sound manner across the state. In January 1997, the Michigan Department of Environmental Quality took a major first step towards fulfilling this deficiency with its report entitled*, A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters*. In order to develop the comprehensive program called for in this report, an ecosystem approach is needed to evaluate simultaneously relationships between trace metals and the air, water, land and biota. The analysis of tree rings, soil profiles or lake sediment profiles could reveal the depositional rates of various elements over time and determine background or baseline concentrations for these elements as well as trends. Lake sediments can provide the history of trace element deposition as well as the biological response of part of the watershed biota. In terms of biomonitoring, many components of the ecosystem could be sampled to document trace element deposition, movement and fate in ecosystems. Three key organisms, raccoons, snapping turtles and fish are suggested for the biomonitoring component for the terrestrial, semi-aquatic and aquatic environments, respectively.

A proposed monitoring program is presented which could result in a better understanding of the movement of toxic trace elements and other substances within, and their impact on, Michigan's environment. Such a program also would be better able to demonstrate the effectiveness of resource management and environmental protection activities and provide predictive tools and options for the management and protection of Michigan's environment.

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INTRODUCTION

In 1986, the U.S. Environmental Protection Agency (USEPA) initiated a program to examine environmental risks to U.S. citizens. Specifically, the federal agency identified critical risks and compared them with each other to develop a hierarchy for remediation and pollution prevention. This hierarchy, based on scientific knowledge, could then be used to design strategies that would yield the most positive results given the funds available. In late 1991, at the direction of Governor John Engler, Michigan became one of the first states to develop a similar relative risk program.

The Governor's Relative Risk Program was initiated in September 1991 with the creation of three multi-disciplined committees composed of scientists, citizens, and representatives of governmental agencies, respectively. The purpose of each committee was to identify and evaluate known and suspected environmental problems, decide which problems were of particular concern, and assign a relative rank to each by comparing the risks it posed to the environment and quality of life. The resulting report, entitled, *Michigan's Environment and Relative Risk* (Rustem *et. al.,* 1992a), was presented to the Governor in July 1992. In his July 17, 1992, issuance of the report to the citizens of Michigan, Governor Engler stated "*I am convinced it is time to carefully review and evaluate our priorities and base those priorities on careful thought and scientific information. We must do this in order to efficiently apply our limited resources to addressing the most serious environmental risks that our state faces*."

The report identified 24 risk issues and ranked each in terms of concern as "high-high", "high", "medium-high", or "medium" (Table 1) The 24 risk issues were subsequently grouped into 19 task forces (Table 2). In the report, "risk" was considered to be any involuntary exposure to harmful substances or conditions outside the workplace. "Relative risks" were considered to be those residual risks remaining after consideration of current environmental control programs.

Trace elements in the ecosystem were ranked as having a "high" risk because of their toxic nature and the limited knowledge of their distribution, concentration, trends, sources, fate and biological impacts. The rational for ranking trace elements as having a "high" relative risk appears in detail in the series of white papers which accompanied the relative risk report (Rustem *et. al.,* 1992b) (Appendix I).

The purpose of this report is to present a conceptual ecosystem monitoring approach that if accepted and pursued will result in a better understanding of the trace element contamination problem within Michigan's environment. This report presents a conceptual and integrated ecosystem monitoring approach with the scientifically based and specific monitoring design and details to be developed following acceptance of the proposed ecosystem approach. A comprehensive ecosystem based toxic trace element monitoring program is recommended in order to evaluate the relationships between trace element deposition and movement and the air, water, land and biota. An integrated ecosystem monitoring program for trace elements could also be used to demonstrate the results of both environmental protection and resource management activities in Michigan.

Mercury, one of the toxic trace elements of most concern, was reviewed in detail for the Governor by the Michigan Environmental Science Board (MESB) in its 1993 report (Fischer *et al.*, 1993). The MESB found numerous data gaps and the need for a scientifically sound mercury monitoring program. The MESB also reported its findings to the Governor on lead, another toxic trace element, and the various routes of lead exposure for Michigan's citizens, with targets for effective remediation (Bulkley *et al.*, 1995). Although these two reports addressed the two elements of primary concern to human health in Michigan, a number of other toxic trace elements are known to have increased in the Michigan environment, along with other toxic compounds and nutrients (LTI, 1993; USEPA, 1994).

Table 1. Identified relative risks issues and rankings.(a)

High-High	High	Medium High	Medium
Absence of Land Use Planning	Point Source Dischargers	Contaminated Sites	Accidental Releases & Responses
Urban Environment Degradation	Air Toxics Deposition	Contaminated Sediments	Acid Deposition
Energy Production & Consumption	Biodiversity/Habitat Changes	Hazardous Waste	Critical Air Pollutants
Global Climate Change	Indoor Air Pollutants	Photochemical Smog	Electromagnetic Field
Lack of Environmental Awareness	Non-point Source Discharges	Solid Waste	
Ozone Depletion	Trace Metals in Ecosystem	High-Level Radioactive Waste	
	Alteration of Surface/ Groundwater Hydrology	Low-Level Radioactive Waste	

(a) From Rustem *et al.,* 1992a.

Many of these trace elements are directly or indirectly related to almost all the other issues ranked in the relative risk report. Trace elements are obviously related to such relative risk issues as Atmospheric Transport and Deposition of Air Toxics; Non-point Source Discharges to Surface Water and Ground Water including the Great Lakes; Contaminated Sites; Contaminated Surface Water Sediments; Generation of Radioactive, Hazardous or Municipal and Industrial Wastes; Point Source Discharges to Surface Waters and Groundwater including the Great Lakes, and Acid Deposition. Other relative risk issues that are less obviously related to trace elements include Degradation of Urban Environments; Energy Production and Consumption; Indoor Pollution and Absence of Land Use Planning that considers resources and the integrity of ecosystems.

Trace elements are accompanied by a number of toxic compounds of concern in the environment. These toxic compounds include pesticides, polynuclear aromatic hydrocarbons (PAH's), chlorinated hydrocarbons and other compounds of sulfur and nitrogen. These compounds, along with the various toxic elements, should be sampled together in Michigan's aquatic and terrestrial ecosystems.

Table 2. Relative Risk Task Forces.[(a)]

Environmental Education
Urban Recreation
Contaminated Sites
Low-Level Radioactive Wastes
Surface Water Sediments
Electromagnetic Fields
Hazardous, Municipal, Industrial & Solid Wastes
Integrated Land Use Planning
Non-point Source Dischargers
Air Issues
Accidental Release & Response
Point Source Dischargers
High Level Radioactive Wastes
Energy Production, Climate Change & Stratospheric Ozone Depletion
Trace Metals in Ecosystem
Biodiversity/Ecosystem Management.
Alteration of Surface/Groundwater Hydrology
Indoor Air
Urbanization & Fragmentation of Agricultural/Forest Land

(a) Relative Risk Task Forces as a function of regrouping of the 24 Relative Risk Issues by the Michigan Natural Resources Commission, 1992.

The Air Quality Issues Task Force (AQITF) recently considered those air quality issues listed in a draft of its relative risk report (Wolff *et al.*, In preparation). The primary focus of this draft report is regulated compounds and includes particulates, acid deposition, ozone, nitrogen oxide, sulfur dioxide, carbon monoxide and hazardous air pollutants, and PAH's. With the exception of mercury, these substances were not considered as posing a significant risk to human health or wildlife. However, the MESB Air Quality Panel in its evaluation of particulate matter and ozone as related to human health documented the controversial nature and current scientific uncertainty of new air quality standards for these substances (Fischer *et al.,* 1997). Although not discussed in the AQITF (draft) report, a number of elements are included in the list of 189 hazardous air pollutants in the 1990 Clean Air Act Amendments. These elements are regulated by the USEPA by imposing maximum achievable technology limits on their discharge and include: selenium, beryllium, cadmium, arsenic, lead, mercury, cobalt, chromium, antimony, manganese, nickel and radionuclides. The Air Quality Division of the Michigan Department of Environmental Quality (MDEQ) regulates the discharge of additional toxic elements on a case by case basis.

ECOSYSTEM MONITORING

The ecosystem concept, as a basic framework for managing or protecting the environment or natural resources, has been recognized for more than 50 years. We manage ecosystems for various products and amenities and will continue to do so in the future as human population demands on natural resources increase. However, an integrated ecosystem monitoring program for Michigan does not exist to guide resources management or protection activities. Monitoring, for the most part, has focused on issues of concern, such as toxics, nutrients, etc. or on outputs of ecosystems, such as forest products, fish, wildlife, recreation, and other amenities. Basically this was the reductionist approach used in the relative risk report, wherein problems were agreed to generally and ranked in some subjective fashion, as if one was not related to the others. This approach has been successful in the past where problems in the environment were obvious and affordable technological solutions available. However, where environmental problems are not obvious and decisions must be made as to where limited funds are to be spent most effectively, understanding relationships of materials and biota in time and space is basic to wise decision making.

This proposed trace element monitoring program recommended by this Task Force would sample various comparable components of a number of selected ecosystems (watersheds) in a five to ten year time frame across Michigan in order to provide trends and baseline conditions of trace elements and a better understanding of the relationships of these elements in ecosystems. At this time it is not a question of whether or not trace elements and other toxic compounds have generally declined in the environment, but rather at what rate these substances are now declining and if biological responses can be observed.

TRACE ELEMENT MONITORING PROGRAMS

In the Great Lakes region, a number of governmental agencies have monitored trace elements and materials in air, water, the terrestrial environment, in food and other biota for more than two decades (Table 3). Other organizations and independent researchers have also contributed to this monitoring effort. A massive amount of data has accumulated over the years as specific problems or issues were addressed. Reductions in nutrients, pesticides, other synthetic organic substances, metals, particulates, etc., have occurred due to regulatory actions, applied pollution control technology or pollution prevention (LTI, 1993).

The Great Lakes and inland waters with their indigenous biota have responded in a positive fashion to pollution control programs. Bird populations, such as eagles and other fish-eating birds have increased dramatically (Brewer, McPeek and Adams, 1991 Brewer and McPeek, 1991; Postupalsky, 1991, Binford, 1991; Giesy, Ludwig and Tillitt, 1994; ICJ, 1993) Excessive plant growth and dissolved oxygen problems in lakes and streams have been reduced and body burdens of toxic materials have likewise decreased in fish and other biota. Some localized areas still exhibit elevated contaminant levels due to past discharges. These local situations need to be monitored by pollution management agencies as they are remediated.

MONITORING FOR TRENDS

Trends in the trace element concentrations can be readily observed in lake and pond sediments, acid bogs and calcareous fens, analyses of tree rings and from terrestrial soil profiles. By sectioning a core or analyzing an individual tree’s growth rings, concentrations of elements can be tracked over time. Measuring and tracking loadings and rates of deposition of trace elements and other materials to a watershed or lake bottom entails a more complex spatial sampling program. In these programs, dating core sections using lead 210, chemical, physical or biological markers are needed to ascertain the deposition rates in these cores with accuracy. This allows precise comparisons of watershed events to the condition of the sediment core (i.e., chemical composition or biological composition) and allows associating historical occurrences to their biological impacts.

Recently, Charles, Smol and Engstrom (1994) provided a lengthy and detailed review for investigating lake sediments. Schell (1986), Glooschenko (1986), Benoit *et al.*

(1994) and others, have utilized peat cores to track air contaminant deposition to acid bogs while Cole *et al.* (1994) used peat cores from a calcareous fen for the same purpose. In acid bogs varying degrees of post depositional mobility of certain elements are known to occur, depending on changing environmental conditions, such as: water levels, oxygen concentrations and redox potentials. Less mobility of airborne particulates apparently occurs in calcareous fens.

Dendrochronology and the dendrochemistry of tree rings is another method to assess changes in trace elements over time that is always available to an investigator. Soils also reflect changes in the deposition of trace elements but in this ecosystem compartment, trace elements can be mobilized by acid rain and move through the soil profile to groundwater.

Table 3. Key federal, state and international governmental organizations that monitor trace elements in air, water, soils, biota and/or food in the Great Lakes ecosystem.

U.S. Department of Commerce	National Oceanic and Atmospheric Administration Great Lakes Environmental Research Laboratory
U.S. Department of Agriculture	Forest Service - Forest Health Monitoring, Natural Resources Conservation Service.
U.S. Department of the Interior	Bureau of Land Management, Geological Survey, National Biological Services, Fish and Wildlife Service.
U.S. Environmental Protection Agency	National Acid Precipitation Network, National Emissions Data System, The Great Waters Program, Environmental Monitoring and Assessment Program (EMAP), Integrated Atmospheric Deposition Network.
U.S. Department of Health and Human Services	Food and Drug Administration Agency for Toxic Substances and Disease Registry
Michigan Department of Agriculture	
Local governmental cooperation with the Michigan Department of Public Health,	
Michigan Department of Environmental Quality	

Monitoring trends of elements in biota provides important data about the actual responses to trace elements exposure. Monitoring the environment without a biological end point does not provide the basic data for sound management decisions. Finding a trace element in the environment at some concentration is insufficient for predicting its biological availability or its effects.

PROPOSED TRACE ELEMENT MONITORING PROGRAM FOR MICHIGAN

This report proposes selection of a series of ecosystems across the state where the air, land, water and biotic components of each ecosystem would be sampled, evaluated and compared. Examination of trace metals and other pollutants in tree rings, soil profiles and sediment profiles would reveal deposition rates as well as background concentrations. Lake sediments, for example, could provide not only a deposition profile but also a measure of the ecosystem response associated with the deposition. Three animal species (fish, turtles and raccoons) could be used as biomonitors to record, statewide, the accumulation and impact of persistent hazardous materials. Correlation of environmental deposition with accumulation in these species would permit an evaluation of the significance of materials introduced into the ecosystem and the response of the system to control or remediation measures.

Recently, the MDEQ prepared a proposed monitoring program for Michigan's surface waters (MDEQ, 1997). In general outline, this is a large complex program involving a number of governmental agencies as well as citizen volunteers and would require considerable coordination. The MDEQ proposed monitoring program would sample many of the same environmental parameters as proposed in this report. However, and as with any monitoring program, additional refinements will be needed over time in order to achieve the level of integrated and focused systems ecosystem monitoring approach called for in this report. It should also be noted that the Michigan Department of Natural Resources (MDNR) is in the process of developing a resource management plan based on the ecosystem concept (MDNR 1997). At this time it is uncertain what parameters might be proposed to be monitored.

As pointed out above, considerable reduction in toxic elements, heavy metals, toxic compounds and other substances, has occurred due to regulatory and pollution prevention activities. In many situations the rate of change will now be much slower than in the past, depending on the substance in question. Under such conditions of low rates of change, detection of change requires an increasingly sophisticated sampling program design, requiring not only more samples but better statistical analysis in order to provide scientifically valid trends, conditions and make future predictions. The shorter the period of testing and data gathering, the better and more thorough must be the sampling and statistical methodology employed. Spacing sampling events over longer time periods, such as five to ten years, would make changes more easily detectable.

Fourteen trace elements are proposed by the Task Force for monitoring in various media: antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, tin and vanadium. These trace elements were selected from a review of the literature of the toxic trace metals and metalloids in plants and animals of the world (Jenkins, 1981). These trace elements have at least some of the following characteristics:

1. Toxic to humans, plants or animals,
2. Widespread and fairly common,
3. Element exposure is sufficient to cause injury or potential injury,
4. Persistent, and/or
5. Increased use or production at least in the past.

Monitoring for these elements would focus on various species of animals and plants, and in selected tissues, where in some instances, elements concentrate or may cause injury. In addition, soils or sediments would be analyzed for trace elements in all the areas where biological monitoring takes place. Monitoring sites would be distributed across the state according to air transport and deposition patterns of sulfates and associated trace elements.

The great uncertainty of determining and predicting biological impacts from chemical or physical measures of air or water alone can be avoided by directly monitoring the resident biota and thus defining critical trace element pathways for human exposure. Measuring a trace element in air, water, sediments or soils will not predict whether they are bioaccumulated, bioconcentrated, biomagnified or biominified. Biological monitoring of trace elements provides data about historical levels, exposure, injury, status or baseline, pollutant pathways and trends, especially when coupled with the simultaneous analysis of soils or sediments at the same monitoring sites.

The organisms selected for biomonitoring should have the following characteristics:

1. Accumulate various elements,
2. Be common,
3. Widespread geographically,
4. Be easily collected,
5. Be of adequate size to permit tissue resampling,
6. Occur in impacted and unimpacted areas, and
7. Show correlations with environmental levels of trace elements.

This proposal provides a conceptual approach to monitoring ecosystems and trace elements and is designed to enhance our understanding of ecosystem function and structure (relationships and rates of change between system components) over time. The proposal is flexible and provides the overall research coordinator considerable latitude to modify this program. Since the proposed monitoring program is to provide scientifically sound baseline data as well as trends, it should be designed and managed by key personnel with both research credentials and past experience in scientific methodology, sampling design and data analysis.

MONITORING SITE SELECTION

Lakes and their watersheds have been proposed as monitoring sites because lakes are in many ways the repository of airshed and watershed history and biological responses. A series of lakes and their watersheds recommended as potential candidates for trace element monitoring are presented in Table 4. Figure 1 shows the distribution of the these lakes by county. Most of these lakes have a considerable portion of their watershed in public ownership, which provides access for sampling, as well as management and protection of the sampling location. The proposed lakes are relatively large and are of such a size to ensure for adequate sized samples for certain organisms. In addition, these lakes and parts of their associated watersheds have a long history of management and past data collection that can assist in planning a monitoring program.

Table 4. Proposed lakes and their watersheds for evaluation as trace element monitoring sites across Michigan.

REGION I (a)

Beaver and Nawakwa Lakes, Alger Co.; Carp Lake, Chippewa Co.; Gogebic, Thousand Island or Clark Lakes, Gogebic Co.; Lac LaBelle and Gratiot Lakes, Keewanaw Co.; Muskallonge Lake, Luce Co.; Lake Independence, Marquette Co.; Indian Lake, Schoolcraft Co.; Brevoort Lake and Twin Lakes (Bois Blanc), Mackinaw Co.; King Lake, Baraga, Co.

REGION II (a)

Black, Burt and Douglas Lakes, Cheboygan Co.; Crooked/Pickerel Lakes, Emmet Co.; Tawas, Loon or Long Lakes, Iosco Co.; Big Star Lake, Lake Co.; Glenn or Lake Leelanau Lakes, Leelanau Co.; Grand Lake, Presque Isle Co.; Higgins or Houghton Lakes, Roscommon Co.; Hubbard Lake, Alcona Co.; Lake Geneserath (Beaver Island), Charlevoix Co.; Pine Lake, Manistee Co.; Long Lake, Wexford Co.

REGION III (a)

Gun and Long Lakes, Berry Co.; Coldwater Lake, Branch Co.; Wamplers and Portage Lakes, Jackson Co.; Gull Lake, Kalamazoo Co.; Lincoln Lake, Kent Co.; Orchard Lake, Oakland Co.; Diamond Lake, Cass Co.; Paw Paw Lake, Berrien Co.; Long Lake, Ionia Co.; Chemung and Bishop Lakes, Livingston Co.; Murphy Lake, Tuscola, Co.; South Lake, Washtenaw Co.

(a) Michigan Department of Natural Resources regional designation.

Although the specific lakes and watersheds recommended have a number of similar characteristics and represent a reasonable geographical distribution across the diverse Michigan landscape (Albert, 1995), a thorough evaluation should be completed with the various state or federal management agencies, as to each lake's history and past management practices and the possibility that the watershed would meet trace element monitoring program goals.

After the appropriate lakes and their surrounding watersheds have been selected, a sampling sequence should be determined. Since the rate of change in the trace element loading has declined along with the concentrations of compounds of concern, detection of real or significant changes over short time periods (< 5 years) could be difficult. Once a lake and its watershed are sampled, and adequately characterized, resampling after five to ten years is probably appropriate. In part, the rates of change observed in trace elements determined from the initial sediment cores samples, could also suggest a possibly more appropriate sampling time frame, either longer or shorter than five years.

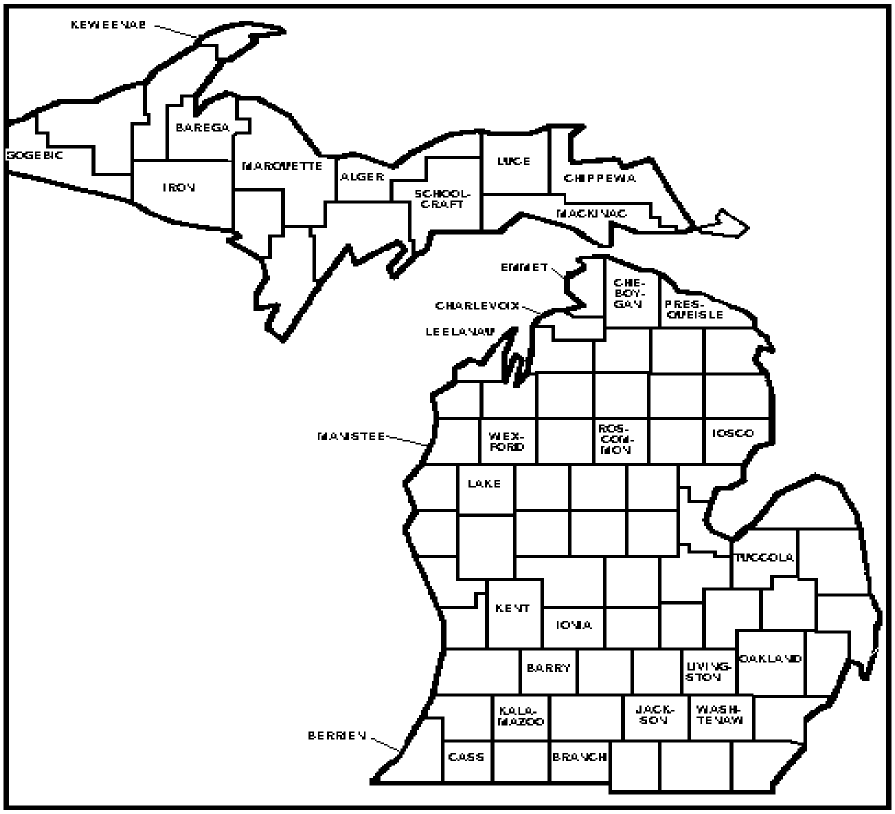

Figure 1. Counties with proposed lakes and watersheds for evaluation as trace element monitoring sites.

BASELINE AND TREND INFORMATION

Baseline or ambient conditions are the basis for future comparisons and predicting or determining trends. In most situations baseline or ambient conditions in the watershed will not be known with any degree of acceptable scientific certainty. Some components of a lake watershed or ecosystem, if properly sampled, yield only baseline conditions over short time frames. These include such things as some plants, animals and most animal population estimates, as well as water, air, surficial sediment and soil chemistry. Other ecosystem components, if properly sampled and analyzed, yield both baseline and trend data. Core samples of lake sediments, peat bogs, soils and trees contain the accumulated history of parts of the system over many years and are always available for resampling. Trends in trace elements can thus be established from core samples from precolonial times to the present (ambient).

Environmental monitoring programs have been extensively criticized because much of the data lack scientific validity. The basic problem with monitoring programs has been the lack of or faulty experimental design (MDEQ, 1996, Rose and Smith, 1992; Ward, 1989, Mar *et al.*, 1986). Although other problems, such as poor sample collection procedures or lack of adequate quality assurance and quality control, may compromise a monitoring program, correcting these problems would not overcome a sampling program design problem. To yield scientifically valid data, a monitoring program must be designed to account for natural and experimental variability. Furthermore, the specific questions to be answered or hypothesis to be tested must be developed and stated before the program is designed and data collection begins in order to provide statistical confidence and validity in any conclusions. In addition to faulty monitoring program design, much of the collected data has not been properly analyzed or in many cases not analyzed at all. Most data summaries contain descriptive statistical measures only.

Terrestrial Ecosystem Monitoring

Compared to the air quality and water monitoring programs, the terrestrial environment has received little attention from regulatory agencies. In recognition of this deficiency, the USEPA, as part of its long term Environmental Monitoring and Assessment Program (EMAP), became a participant in the Forest Health Monitoring (FHM) program of the U.S. Department of Agriculture's Forest Service along with other cooperators. A field methods guide for the FHM was developed cooperatively and its table of contents appears in Appendix II (Conkling and Byers, 1993). Trace elements were to be measured in soils, foliage, stemwood and twigs and lichens. Other forest characteristics that were to be measured that might be affected by trace element deposition included root disease, vegetation structure and photosynthetically active radiation (PAR). At this time, surveys of lichen communities on 126 plots have been initiated. Funding for chemical analysis of these lichen samples at this time is questionable. Funding for both EMAP and FHM have been greatly reduced or eliminated since 1993.

If at some future date, funds for monitoring trace elements in forests become available, the analyses of growth rings (dendrochonolgy-dendrochemistry) of trees and soil trace element profiles would probably be the best way to monitor trends in forests (Lewis, 1995). Understanding how trace elements move through forest ecosystems to aquatic ecosystems would require implementation of an integrated ecosystem based monitoring program including a number of additional forest ecosystem components.

Aquatic Ecosystem Monitoring

In January 1997, the MDEQ Surface Water Quality and Land and Water Management Divisions published a report entitled, *A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters* (MDEQ, 1997). The monitoring program presented in this report includes several monitoring activities which address trace elements in the aquatic ecosystem. The monitoring activities discussed in this report which are particularly encouraging to the Task Force include: Native Fish Trend Monitoring, Caged Fish or Mussel Studies, Spottail Shiner Monitoring, Water Chemistry Trend Monitoring, Tributary Loadings, Sediment Chemistry Trend Monitoring, Biological Integrity Trend Monitoring and Wildlife Contaminant Monitoring (i.e., bald eagles, mink, herring gull eggs and snapping turtles).

Lake sediments, like tree rings and soil profiles of trace elements, reflect the depositional changes in trace elements and other substances to the watershed. Sediments contain an integrated history of terrestrial events as well as the biological and chemical responses in the lake to those terrestrial events (Figure 2). The study of lake sediments is one of the best and often the only way to obtain historical data. High quality monitoring data can be obtained from the sediments over an extended time period. Chemical profiles of lake sediment cores are intrinsically less variable than most other types of environmental samples including those from water, air, or biota. Since sediment cores reduce sample variability while incorporating long term watershed events, they are an ideal environmental indicator that can be used statewide to assess current as well as past conditions.

Charles, Smol and Engstrom (1994) reviewed the paleolimnological approaches for monitoring aquatic ecosystems and the large suite of biological and chemical indicators available to assess past environmental conditions and rates of change. Schindler (1987) discussed the problem of detecting ecosystem responses to anthropogenic stress. Forested terrestrial ecosystems exposed to airborne pollutants have reduced primary production (growth, PAR) compared to aquatic ecosystems. In aquatic ecosystems, phytoplankton species respond through species composition changes with a loss of sensitive species as well as changes in the benthic community, which occur rather quickly. These preserved biological changes are preserved for every lake and can be detected in the lake sediments. These changes can also be closely matched with corresponding time scales, as indicated earlier.

Selected Animals for Monitoring Trace Elements

The three animals that meet the criteria previously set forth and which are proposed to serve as trace element biomonitors include raccoons, snapping turtles and fish (more than one species).

Raccoons - In a recent study carried out in Michigan, adult raccoons have been shown to accumulate pesticides, related chlorinated compounds and heavy metals (Herbert and Peterle, 1990). Juvenile raccoons had lower levels of contaminants. These warm blooded vertebrates feed at various trophic levels in both the terrestrial and associated aquatic ecosystems of their home ranges and are common throughout Michigan.

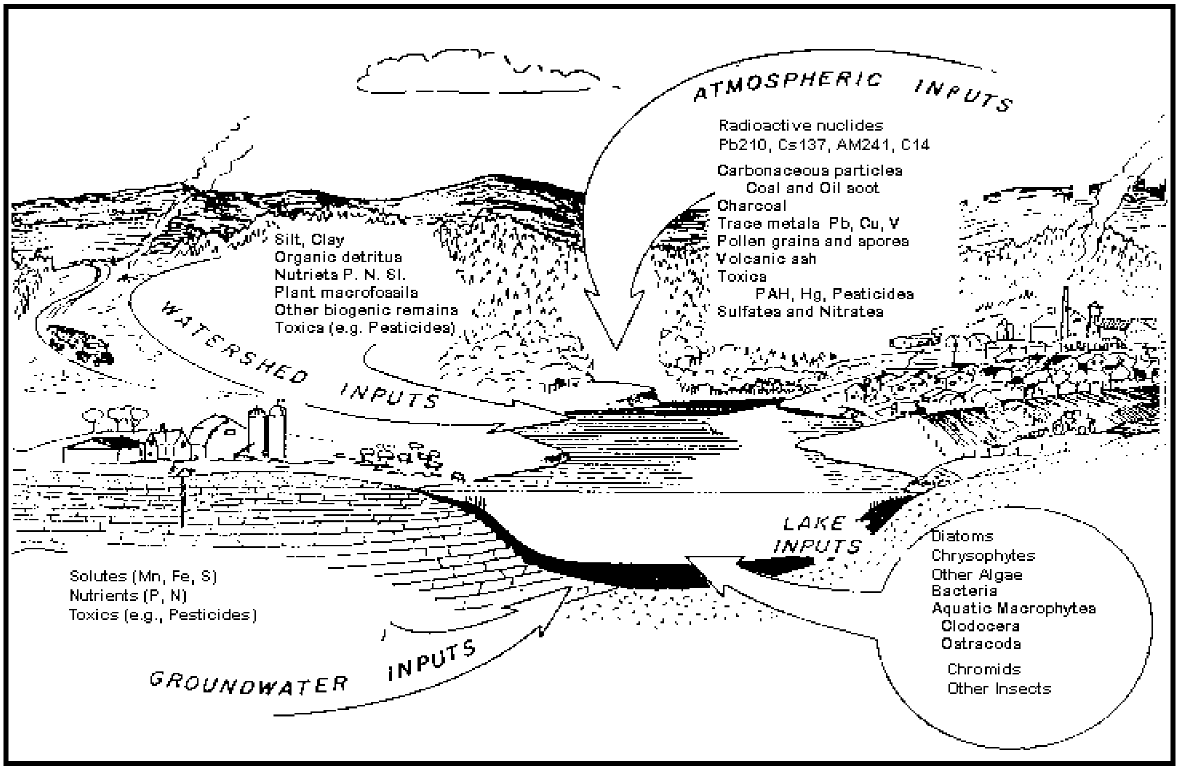

Figure 2. Common components of lake sediment and their sources.

Snapping Turtles - Like raccoons, snapping turtles have been found to accumulate environmental contaminants. Overman and Krajick (1995) found snapping turtles to accumulate lead in the vicinity of lead mining activities but lead in tissues did not appear to affect turtles. Pesticides, chlorinated hydrocarbons and heavy metals also have been found to accumulate in snapping turtles and their eggs (Helwig and Hora, 1983; Struger *et al.*, 1993; Bishop, Carey and Brooks, 1989). Snapping turtles, like fish-eating water birds, appear to be sensitive to environmental contaminants during embryological development in the eggs (Bishop, Carey and Brooks, 1989). Collecting clutches of snapping turtle eggs allows an investigator to measure contaminant concentrations, abnormal embryological development and hatchability, parameters that are difficult to assess in either raccoons or fish.

The omnivorous snapping turtle has a home range of a few hectares and has a diet of about one-third fish, one-third vegetation and one-third miscellaneous. Like the raccoon, snapping turtles are common throughout Michigan and easily trapped.

Fish - Analysis of contaminants in fish has been a major focus of environmental organizations because of their importance as perhaps the primary source of contaminants to humans and animals, dependent on fish as a major food. Most of the fish contaminant monitoring in Michigan has been carried out to ascertain if fish muscle tissue has contaminants of concern above federal and state regulatory consumption standards or criteria. The data are usually presented only as concentrations of selected contaminants in a limited number of fish of various predator or benthic species. This fish sampling program has not been based on an understanding of fish contaminant concentration variability, fish species variability or the factors correlated with contaminant variability. Therefore, a great deal of unexplained variability currently exists in the data gathered by the fish contaminant monitoring program. Further analysis of the accumulated fish contaminant data, wherein variability within and between water bodies can be determined and statistically quantified is needed. The necessary determination of this variability, using appropriate statistical measures would also aid in selecting specific lakes and watersheds for trace element monitoring and determining overall sampling strategies to answer those questions of concern with statistically defensible methods and analysis.

Analysis of mercury in fish tissue from lakes in the Great Lakes region suggests some methods for the analysis of fish contaminant data and designing a trace element monitoring program (Sorensen *et al.*, 1990; Wren *et al.*, 1991; Parks, Craig and Ozburn, 1994). The sources of variability that have been encountered in fish monitoring programs are also discussed and correlated with contaminants reported in these and other published reports.

SUMMARY AND CONCLUSIONS

Toxic trace elements are only one class of substances that have been widely dispersed in the environment due to human activities. Toxic organic and inorganic compounds have accompanied these trace elements. Concentrations of most of these toxic substances have declined over the past 25 years in the Great Lakes region due to regulations and conservation.

Michigan currently does not have a comprehensive program to monitor toxic trace elements in a systematic and scientifically sound manner across the state. In January 1997, the MDEQ took a major first step towards fulfilling this deficiency with its report entitled*, A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters*. In order to develop the comprehensive program called for in this report, an ecosystem approach is needed to evaluate simultaneously relationships between trace metals and the air, water, land and biota. The analysis of tree rings, soil profiles or lake sediment profiles could reveal the depositional rates of various elements over time and determine background or baseline concentrations for these elements as well as trends. Lake sediments can provide the history of trace element deposition as well as the biological response of part of the watershed biota. In terms of biomonitoring, many components of the ecosystem could be sampled to document trace element deposition, movement and fate in ecosystems. Three key organisms, raccoons, snapping turtles and fish are suggested for the biomonitoring component for the terrestrial, semi-aquatic and aquatic environments, respectively.

A comprehensive monitoring program called for by the Task Force will need to be based on sound ecological principles and should include among its staff experienced systems ecologists in order to ensure a more thorough evaluation and understanding of the interrelationships and intrarelationships of the biotic and abiotic components of the ecosytems monitored. Such a program would result in a better understanding of toxic trace elements and other substances, and their movement and impact on Michigan's environment. Such a program also would be better able to demonstrate the effectiveness of resource management and environmental protection activities and provide predictive tools and options for the management and protection of Michigan's environment.

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APPENDIX I

TRACE METALS IN THE ECOSYSTEM

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TRACE METALS IN THE ECOSYSTEM

“And when there is mining for veins of gold and silver
Which men will dig far and deep down in the earth
What stenches arise, as at Scaptensuls!
How deadly are the exhalations of gold mines!
You can see the ill effects in the miners' complexions.
All these exhalations come from the earth
And are breathed forth into the open light of day.”

Lucretius (96-55 BC)
(*De rerum natura*, Book VI)
(from Nriagu, 1990)

“All organic substances are eventually biodegradable, except the great class of plastics.... Not so for metals. No metal - or element - is biodegradable. If released into the environment, all metals will accumulate until they are leached out of soil to enter the sea [also large lakes]. In the sea [also large lakes] they tend to fall to the bottom. If in the process they enter the body of man, they may do good or harm. It is hard to get rid of them. Too little attention has been paid to them. For this reason they are important.”

Henry A. Schroeder, M.D. (1974)

"Because chemical loading of the environment can occur long before effects are observed, the term *chemical time bomb* has been coined to describe such phenomena."

William M. Stigliani, et al. (1991)

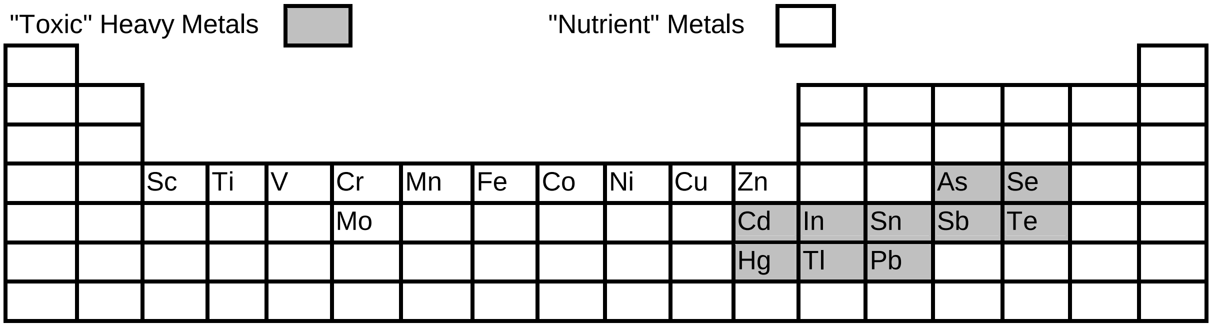
Problem

This white paper addresses the issue of trace metals in the environment. The discussion that follows is not meant to be an exhaustive survey of metals in the environment. Such surveys can be found in recent works such as that of Fergusson (1990). Rather, the aim of this paper is to examine why there is a concern about metals in the Michigan environment and the Great Lakes region as a whole and some of the problems associated with understanding pathways and fates of metals in the environment. The paper is presented in five sections that discuss (1) the issue, (2) the source of the problem, (3) time and space scale of problem (4) recovery time, and (5) risks. The paper then concludes with an overall summary and suggestions.

Issue

Trace metals are metals and metalloids (e.g., lead and arsenic, respectively, see Figure 1) that typically occur in low concentrations in the major elemental reservoirs of the earth: sediment, soil, rocks and minerals, water, air, and biota. The problems associated with trace metals in the environment, as summarized in the above quotations, are: metal contamination has occurred since ancient times and has caused health effects; metals cannot be destroyed, are hard to remove from the environment, and can be concentrated; and not addressing the issue [in part stemming from a lack of knowledge] could result in serious consequences.

Figure 1. Selected metals discussed in text



Some of these metals such as the "heavy" metals arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) are toxic even at low concentrations. Hence, the International Joint Commission (U.S.and Canada) has targeted these four metals (along with 10 organic compounds) as critical contaminants in the Great Lakes region (e.g., Colborn et al., 1990).

However, with increasing concentration in the environment, metals not normally toxic, and even essential to life at low concentrations, become toxic. Such is the case for the "transition" metals titanium (Ti), vanadium (V), chromium (Cr), nickel (Ni), cobalt (Co), and copper (Cu).

Thus, there are potentially more trace metals (both heavy and transition) and forms (oxidation state, methylated, etc.) of the metals that may be of concern in the Great Lakes region than the four "critical" contaminants. The list of these metals might include V, Cr (IIL VI), Co, Ni, Zn, Mo (molybdenum), Cd, Hg (0, ionic, methylated), In (indium), Tl (thallium), Sn (tin), Pb (ionic and methylated), As (ionic and methylated), Sb (antimony), Se (selenium), and Te (tellurium).

The earth is a dynamic system and these elements are moved naturally from one reservoir to another. The movement of an element among the reservoirs in the ecosystem is the biogeochemical cycle of the element. Anthropogenic activities have disrupted the natural cycles of many elements. For example, the world's population consumes approximately $1.0 * 10^6$ kg of mineral resources per person per year. The emission of trace elements associated with this consumption ($50 * 10^{15}$ kg/y) exceeds the natural global supply of trace elements as represented by the amount of minerals transported to the ocean via sediments in rivers ($17 * 10^{15}$ kg/y) (Apsimon, et al. 1990). This disruption of biogeochemical cycles has resulted in decreased elemental abundances in the rock-mineral reservoir and in increased abundances in the "environmental" reservoirs soil, water, air, and biota. This has increased the risk for the interaction of humans and other biota with trace metals (Apsimon, et al. 1990).

The issue of trace metals in the environment is part of the broader concern of environmental geochemistry and health and disease. This is the study of the relationship of the chemistry of drinking water (from ground water, river, lake), soil, plants, animals, and air to geographic patterns of health and disease. The scope of this issue is multi-disciplinary, involving atmospheric scientists, geologists, ecologists, geochemists, MDs, dentists, hydrogeologists, soil scientists, and biologists. Hopps (1974) presents an excellent introduction to these studies. The Society for Geochemistry and Health (SGH) links these researchers to study topics such as F (fluoride) and arsenic in drinking water (Rajagopal and Tobin, 1991; Varsanyi, et al., 1991) Pb in the diet (Sherlock, 1987), Cd concentrations in soils in cities (Mielke, et al., 1991), Pb in house dust (Laxen, et al., 1988), and accumulation of metals in workers (Hewitt, 1988). The papers presented in the journal of SGH (Environmental Geochemistry and Health) show that the issue of trace metals in the environment is being addressed by other countries and other regions of the U.S.

Some of the problems with trace metals in the Michigan ecosystem are obvious. Ingestion of leaded paint by children, mercury in fish throughout the midwest, and arsenic in ground water in the Bad Axe area are a few examples. Other problems, such as the continual build-up of metals in soil, are not as obvious. The geochemistry of trace metals (and other elements as well) in the Michigan environment and how this geochemistry relates to health and disease is poorly understood. This lack of knowledge continues to load the *chemical time bomb*.

Developing solutions to deal with this problem rests on understanding the local, regional, and global scales of this problem; an understanding of sources; the biogeochemical cycles of the elements; and the toxicity and synergism of trace elements. Our efforts in developing solutions are complicated by the fact that there are natural as well as anthropogenic sources for these elements; these elements can be reintroduced into the environment after what might have appeared to be their permanent removal; and total elemental concentrations in either the solid phase or aqueous phase may not indicate an element's bioavailability.

Source of the Problem

Of major concern is the build-up of metals in the environment due to anthropogenic emissions, mainly from fossil-fuel combustion, waste incineration, manufacturing processes, mining, and smelting. The relative importance of these sources varies for each metal This is illustrated on Table 1 for the big four metals As, Cd, Hg, and Pb.

Table 1. Anthropogenic emissions and crustal abundance of As, Cd, Hg, and Pb. Emission units are in 10^6 g/year. (Wilber et al., 1992) and crustal abundances are in μg/g (Fergusson, 1990). Interference is calculated as emission rate / crustal abundance. Data for Pb oil, motor fuel, industry, and solid waste disposal from EPA (1990). Boxes highlight significant sources for metal.

SOURCE	ARSENIC	CADMIUM	MERCURY	LEAD
COAL	931.0	80.7	132.4	778.0
OIL	19.8	25.7	6.4	50.0
MOTOR FUEL		14.7		2,200.0
NON IRON SMELTING	365.8	46.4	51.0	
WASTE INCINERATION	2.7	20.7	104.0	
IRON/STEEL PRODUCTION		113.0		
INDUSTRY	36.3	?	355.6	2,200.0
SOLID WASTE DISPOSAL				2,200.0
MINING	17.4			?
PESTICIDE USE	1,500.0			
TOTAL ANTHROPOGENIC	2,873.0	199.5	649.7	7,428.0
CRUSTAL ABUNDANCE	1.8	0.11	0.05	13.0
INTERFERENCE	1,596	1,814	12,994	571

The major anthropogenic sources for As, Cd, Hg, and Pb are historical pesticide use, coal burning, iron/steel production, and motor fuel/industry, respectively. There have been some significant changes in the relative importance of these sources recently, which the table does not indicate. For example, the amount of Pb emission from motor fuels in 1981 was 15,400 * 10^6 g/year, which would have made this source the most important (EPA, 1981). However, the table does show that even if the major sources were eliminated, there are significant other sources for the metals. For example, if industrial emissions of Hg were eliminated, coal burning would still contribute a large amount of Hg to the ecosystem. What is important to realize, however, is that anthropogenic emission of trace metal to the environment is not the only source for the metals. Natural processes also contribute to the flux of trace metals to the environment.

These natural sources include the weathering (chemical breakdown) of minerals in sediments (e.g. glacial till) and rock (e.g. iron formations in the Upper Peninsula), and degassing of volatile elements such as Hg from the crust. One of the most significant differences in understanding trace metals in the environment as compared to toxic organic compounds is that toxic organic chemicals have few, if any, natural sources.

Mercury is a good example of the importance of natural trace metal emissions to the ecosystem. The anthropogenic emission rate for Hg is 649.7 * $l0^6$ g/year and the natural emission rate is 1018.5 * 10^6 g/year, the latter accounting for 61% of total emissions. Thus, even if we were to eliminate anthropogenic emissions of Hg, there would still be a significant natural source for the element.

Anthropogenic activities are, however, significantly affecting the biogeochemical cycle of Hg. For example, a crude anthropogenic interference index can be calculated (ignoring units) as the emission rate divided by the crustal abundance (Table 1). Crustal values are used as the normalizing number because the crust is the ultimate natural source for metals in the ecosystem. Except for Hg, the relative magnitudes of the interference number among the metals are similar. According to these calculations, anthropogenic activities are affecting the Hg biogeochemical cycle by an order of magnitude more than the other metals.

The east-north central states (Michigan, Wisconsin, Illinois, Indiana, and Ohio) are a major source for and recipient of trace metals. This is demonstrated by comparing emissions rates of this region to other regions on Table 2.

Table 2. Relative anthropogenic emission rates of selected metals for the U.S. (from Wilber et al., 1992). Values in %.

STATES	**As**	**Cd**	**Hg**	**Pb**
New England	0.5	3.0	1.7	4.3
Middle Atlantic	4.3	6.9	4.4	11.9
East-North Central	12.3	17.3	5.7	16.6
South Atlantic	11.4	7.9	8.2	14.6
East-South Central	7.7	7.2	3.5	5.9
West-North Central	2.3	11.7	6.7	6.3
West-South Central	4.1	20.1	6.1	10.6
Mountain	10.3	18.0	27.2	5.4
Pacific	0.9	2.1	13.2	11.6

Trace metals enter the Michigan ecosystem both from within the state and from outside Michigan borders (trans-boundary effect; see Somers, 1987). Mercury emission from the east-north central states is relatively low compared to the other areas, yet mercury has been identified as a critical pollutant in this region. One could infer from this that (1) trans-boundary input of Hg may be important, (2) Hg may have a high natural emission rate in this area and (3) Hg is probably a critical contaminant in other regions as well.

Further evidence of the potential trans-boundary problem of metals in the Michigan ecosystem is demonstrated in Table 3. This table shows the relative volumes of hazardous wastes contributed by Great Lakes states and provinces. Point and non-point sources include waste isolation (leakage from landfills and waste incineration), mining activities (extraction, tailings leachate, smelting), industrial leakages (e.g., paint manufacturing, tanning, paper mills), agriculture, (e.g., metal-bearing pesticides), and energy generation (burning of the fossil fuel: oil, gas, coal). Although Michigan generates a significant amount of waste, only two of the Great Lake states are much higher.

Table 3. Hazardous Waste generation in the Great Lakes Region (Colborn, 1990).

STATE/PROVINCE	**WASTE**
	10^6 g/year
Illinois	2.3
Indiana	2.0
Michigan	**3.5**
Minnesota	0.4

New York	14.5
Ohio	3.7
Ontario	3.6
Pennsylvania	26.4
Wisconsin	0.1

Pathways for trace metals in Michigan and the Great Lakes region in general) are: atmosphere to land and water (Great Lakes, inland lakes, rivers); from land (that which is added from the atmosphere and that from the weathering of minerals) to ground water and rivers, and from ground water and rivers to the Great Lakes (as well as inland lakes). The Great Lakes themselves therefore might be considered the ultimate "sink" for trace metals. Although data are scarce, recent mass balance modeling for Pb in the Great Lakes ecosystem indicates that the atmosphere may be the major “source" for this metal (Strachan and Eisenreich, 1988). This could be true for the other metals as well. Current research (Eisenreich, et al., 1991) is attempting to address this problem for Pb, As, Hg, and Cd. Little is known about the other trace metals.

Time and Space Scale of the Problem

The use of metals is a reward of humans (Apsimon, et al., 1990). Hg and Pb were being mined and used in ancient times (pre-Roman) (Aitchison, 1960). This of course led to early local pollution. The Greek historian and military leader, Xenophon (430-355 BC), for example, thought that the silver mines in Laurion (Greece) were too polluted to allow a son of a friend to visit the city. (Book 3, Verse 6). The health effects of emissions from mining activities were written about by the Roman poet, Lucretius (see poem at beginning of paper). Vitruvius (I BC), a Roman architect and engineer, commented on extensive water pollution around mines (Book 8, verse 3). As part of his naturalist observations, Pliny (23-79 AD) was concerned that the emissions from mining activities were unhealthy to all animals (Book 33, verse 31). It is now clear that these early mining activities severely contaminated local environments (Livette, 1988).

By the 16th century metal emissions from smelters in Britain were affecting the regional environment (Livett, 1988). During the 17th century this pollution began to affect central Europe and remote regions of Scandinavia (Davis, et al., 1983). Today, trace-metal pollution is truly a global problem ranging from the Arctic to Antarctica (Ng and Patterson, 1981; Boutron, 1986; Davidson and Nriagu, 1986; Boutron and Patterson, 1987; Livett, 1988).

Anthropogenic activities are moving metals among reservoirs faster than natural processes. This has resulted in the perturbation of the natural global cycling of trace metals. As early as 1973 and with limited data, Garrels, et al. (1975) demonstrated this effect by comparing mining production, metal emission rates to the atmosphere by human activities, world-wide atmospheric rainout, and total stream load (used as a measure of the "natural" flow of metals). They found that mining production of metals approaches or exceeds the stream load and that emission rates are within an order of magnitude of the stream load. By comparing emission rates with atmospheric rainout rates it was clearly demonstrated that human activities have a profound effect on the natural cycle of the trace metals. Recent calculations by Nriagu (1990) support the results of Garrels, et al. (1975). Anthropogenic emissions are comparable to or greater than natural emissions for most metals.

Such global emissions are not without consequence. Table 4 (from Fergusson, 1990) shows that a significant number of people have been adversely affected by the trace metals Pb, Cd Hg, and As. The toxicity of all metals released to the environment by anthropogenic emissions exceeds the combined toxicity of all radioactive and organic wastes (Nriagu and Pacyna, 1990). What is also important here is that metals are nondegradable. This further differentiates metals from organic contaminants that can degrade in the natural environment to safe compounds, and also from radioactive wastes that decay into safe elements. Metals can accumulate in the environment and have been doing so for a long time.

Table 4. Magnitude of metal poisonings (Fergusson, 1990).

Element	**Production 1985 1000 t**	**Global Emissions-Air**	**Global Emissions-Water**	**Global Emissions-Soil**	**People Affected**
Pb	4100	332	138	796	>1 billion
Cd	14	7.6	9.4	22	0.5 million
Hg	6	3.6	4.6	8.3	80,000
As	50	18.8	41	82	100,000s

The continual build-up of trace metals in the environment will eventually become stressful to organisms as safe environmental thresholds are exceeded (Apsimon, 1990). These thresholds may have already been exceeded in some environments, but as yet have gone unrecognized (Nriagu, 1988). This leads to the concept of *Chemical Time Bomb* as discussed by Stigliani, et al. (1991).

The concept of *Chemical Time Bomb* (CTB) is quite simple. The environment has a capacity to absorb toxic metals (as well as toxic organics), the major chemical sinks being soils and sediment (rivers, lakes, and oceans). As long as these chemical sinks maintain the capacity to store and thus immobilize the toxic metals, the effects of pollution are significantly reduced. However, if the amount of metals added exceeds the storage capacity or if the storage capacity is reduced because of some environmental change (such as from microbial processes, acid rain, or global climate change), then serious environmental damage can result. For example, microbial processes were involved in the outbreak of Minamata disease (Hg poisoning) in Japan (Davies, 1991) and acid rain in mobilizing trace metals into the ecosystem in eastern Europe (Stigliani, et al, 1991). Changes in the storage capacity of the environment as a result of global climate change are yet to come, but could be anticipated (Apsimon, 1990). Setting off the CTB can result in serious, unanticipated environmental problems which may be more severe than conventional pollution.

The CTB problem adds a new twist to the issue of trace metals in the environment. On the one hand we are and must be concerned with the immediate problems such as Hg in fish, Cu in Torch Lake, and Hg emissions from paper mills. However, the CTB concept adds the dimension of time by considering future problems due to overloading or reduction of the storage capacity of the environment. Consider the following problem. Soils are an important sink for metals supplied to the terrestrial environment from the atmosphere (Apsimon, et al., 1990). Since the atmosphere may be the major source for metals in Michigan it is likely that soils would be strongly impacted. If the storage capacity of the soils were exceeded or reduced then metals would be released to the Great Lakes. A matter of concern is that knowledge of this storage capacity, the length of time for overloading, or sensitivity of the storage capacity to environmental change is lacking. Michigan does not have a program to address the terrestrial (i.e. soil) system.

The CTB concept puts trace metal pollution on the same scale as global climate change and thus giving such pollution more urgency than previously taught. CTB as applied to trace metals is characterized by the following:

- metals released to the environment may have harmful effects on the ecosystem;
- there is a time delay between chemical accumulation and the resulting adverse effects;
- metals may be suddenly released to the environment rather than a slow build-up; and
- environmental systems do not behave naturally when metal-safe thresholds are exceeded.

Recovery Time

Another aspect of assessing the risk of excessive trace metals in the environment is determining how long it will take the ecosystem to recover if imported metal inputs are reduced. Since metals are a natural component of the environment, they cannot be completely removed. Therefore, the first task is to define a clean environment with respect to trace metals. To accomplish this, it is necessary to know the natural concentrations of metals in the environment, i.e. the concentrations that existed before industrial activity.

Determining natural concentrations in the various reservoirs is difficult for most metals since these levels no longer exist (this is especially true for As, Cd, Hg, and Pb). In addition, since the natural abundance of a metal is frequently very small (e.g., lead in natural fresh water), even minor contamination of samples during collection or analysis can give misleading results.

One way of estimating natural levels is to measure trace metal concentrations in remote environments such as the Antarctic. Another approach is to measure background concentrations. For example, deep samples from ice and peat cores can be used to estimate metal concentrations in ancient atmospheric deposition, and sediment cores, to estimate terrestrial + atmospheric deposition of elements to lakes (and oceans).

Knowledge of natural concentrations is important in developing legislation to deal with metals in the environment. For example, if total metal concentrations are used when determining "safe" exposure levels and natural versus anthropogenic concentrations are not differentiated, then it is quite possible that legislation could be enacted that could act to regulate or remediate natural environmental concentrations of a metal.

Assessments of metal pollution based on total concentrations also may be misleading because metals exist in different forms in solution or sediment and each form will control metal bioavailability and toxicity (Jenne and Luoma, 1977). For example, metals can be made significantly more toxic by changes in their oxidation-reduction state in the environment. Chromium is significantly more toxic as Cr (VI) than it is as Cr (III) (NAS 1974). Arsenic (III) is more toxic than arsenic (V) (Fergusson, 1990). The methylation of metals and formation of methyl-metal complexes can significantly increase the toxicity of metals. Mercury as methyl-mercury species (CH_3Hg+) is more toxic than as the ionic species Hg^{2+} (D'Itri, 1972). Other metals that can become methylated include Sn, As, Te, Se, Tl, and Pb (Stumm and Morgan, 1981). Metal complexes with other organic compounds and inorganic ligands (e.g., Cl^-) can reduce metal bioaccumulation and toxicity (e.g., Dodge and Theis; Giesy, et al., 1983).

Adsorption onto particles is a major control on metal cycling in ecosystems because the process removes metals from the water column of lakes and rivers and from ground water and reduces metal bioavailability (e.g., Sigg et al., 1988; Domencio and Schwartz, 1990, Rudd and Turner, 1983). Particles in sediments and soils are composed of a variety of organic and inorganic phases to which metals can be absorbed. Each phase has a different effect on the bioavailability of metals. For instance, metals associated with clays may be more bioavailable than metals associated with organic matter (Luoma and Bryan, 1982; Swartz, et al., 1986). Differences in the form of metal in sediments could cause some lakes with metal pollution to maintain a good fishery, while other polluted lakes to have a damaged fishery. Thus, knowledge of the form(s) of metals in solution soils and sediments is important in legislative decisions.

Another problem in defining how long recovery will take is that there are processes within terrestrial and aquatic systems that delay the cleaning process. For example, soils may continue to be a source of metals to the Great Lakes, even after anthropogenic emissions are reduced. Another example is the delay to the cleaning process in the Great Lakes. A research group at M.S.U. (e.g. McKee, et al., 1989; Matty, 1992) has been studying the cleaning process for metals in the Great Lakes. They have found that trace metals are removed from the lake ecosystem by becoming buried in the bottom sediments. However, the removal process is not 100% effective. Various amounts of metals are released from the bottom sediment before they can be permanently buried. The fate of the released metal is not well defined, but the process will delay the recovery of the lakes. These metals will continue to "bleed" into the lake environment for some time after anthropogenic emissions are reduced. And, until the anthropogenically derived metals are permanently buried in the lakes, the lake sediments themselves may be a major source of trace metals to the ecosystem (Salomons, et al., 1987).

Table 5 presents rough estimates of the range of times for various environmental reservoirs to rid themselves of metal pollution and obtain background concentrations. These times do not consider the effects of CTB or of delay processes such as described. The CTB effect would "quickly" move metal pollution from one reservoir to another. Estimates are based on data for various metals on transfer rates among reservoirs and amount of metals in the reservoirs. The only biological factor taken into account is the half-life of heavy metals in humans. Data were taken from Fergusson (1990), Garrels et al. (1974), Fergusson (1982), Long (1985), Stumm and Morgan (1982), and Strachan and Eisenreich (1988).

Table 5. Estimated times for various environmental reservoirs to rid themselves of metal pollution and obtain background concentrations. Based on natural rates.

RESERVOIR	**TIME TO CLEAN**
REMOVAL MECHANISM	
HUMANS	0.15 to > 100 years
Excretion	
GREAT LAKES - WATER	hours - days - years
Scavenging by particles, flushing	
GREAT LAKES - SEDIMENT	10 to 100 years
Burial	
GROUND WATER	minutes to 10,000 years
Adsorption by particles	minutes to days
Flushing	1,000 to 10,000 to 100,000 years
AIR	hours to days
Wet and dry deposition	
SOIL	100 to 1,000 to 10,000 years
Erosion, leaching, biologic removal	

These data suggest that the time for environmental cleaning could be very long; that is, if we were to stop polluting today (both within state and trans-boundary), the environment would not be clean "tomorrow."

Risks

The health effects of "nutrient" trace metals (Figure 1) have been known for some time (e.g., Hoops, 1977). Adequate Zn intake helps to protect against Cd poisoning. Low levels of Cu can increase the risk of atherosclerosis. Copper is necessary for the utilization of iron and helps to counter toxic effects of Cd and Pb. Chromium deficiency interferes with glucose metabolism resulting in diabetic like symptoms. These and other nutrient metals become poisons in relatively high concentrations. Copper concentrations of 5 to 25 µg/l are lethal to some fish. (Hodson, et al., 1979) and may have caused the tumors in fish in Torch Lake. The exact cause of the tumors is still unclear, however (Evans, 1990). High concentrations of Zn and Cr promote cancer (Babich, et al., 1985; NAS, 1974).

Some metals such as As, Pb, Hg, and Cd have no beneficial health value and can cause certain adverse effects at very low levels. Exposure to these metals is associated with cardiovascular diseases, carcinoma, reproductive impairments, brain and other organic damage (Furgesson, 1990, Nriagu, 1988). These health problems can be considered the extreme effects of interactions with heavy metals. However, adverse effects from low-level exposure to toxic heavy metals may be more subtle, such as neurological effects that could lead to learning difficulties.

Sherwin (1983) defined health as “...a state where there has not been an inordinate loss, reversible or irreversible, of the structural and/or functional reserves of the body." Further, adverse health was defined as "the causation, promotion, facilitation, and/or exacerbation of structure and/or functional abnormality, with the implication that the abnormality produced has the potential of lowering the quality of life, contributing to a disabling illness, or leading to a premature death." Nriagu (1988) draws from this that a significant portion of the “well” population may be suffering from metal poisoning without knowing it. These health effects would be sub clinical (e.g. unrecognized lesions) and/or depletion of function or integrity of cells or organs.

As an example, low levels of Pb can cause metabolic disorders and tubular proteinuria in kidneys. In most cases, the early signs of metal intoxication are unclear and could be masked by other health problems.

In sum, health risks of trace elements in the environment are:

Humans-

- High levels of "nutrient" metals can cause adverse health effects
- Low and high levels of "toxic" metals can cause adverse health effects
- Many people could be suffering from metal poisoning and be unaware of the symptoms

Aquatic and Land Biota-

- Poisoning
- Tumors
- Bioconcentration in food chain and pathway to humans

In addition to health risks associated with metals in the environment there are possible economic risks. Economic planning with respect to the environment is almost always short-sighted. Soils and sediments are considered large reservoirs that will store and eliminate metals from the environment forever. This type of planning ignores the problems associated with the long-term build-up of metals in the environment. Stigliani, et al. (1991) suggest that if long-term economic planning does not take into account the potential impacts of CTB, then it may be difficult to ensure ecological and economic sustainability.

Conclusions

Summary

Local, regional, and global biogeochemical cycles of heavy metals have been disrupted. The result is that humans and other biota have a greater chance of being exposed to high levels of metals. At high levels, some normally nontoxic metals such as Cr and Ni could become toxic, adding to the environmental pool of toxic metals such as Pb and Hg that have no beneficial effects in humans or aquatic and terrestrial biota.

As the heavy metal burden in the environment (air, soil, and water) increases, the threshold level at which "safe" environments become poisonous is approached. This threshold level for most metal-environment-biologic interactions is poorly understood, in some environments has already been surpassed (and may be unrecognized), and could be lowered suddenly by changes in the environment due to such factors as acid rain and global climate change. Assessments of metal pollution based on total concentrations in soils, sediments, etc. may be misleading because metals have many sources and have different toxicities as a function of their form in the environment. Emission inventories for the region indicate that metal pollution could be a problem in Michigan. Delay in addressing the issue of heavy metals in the environment loads the Chemical Time Bomb.

Possible Courses of Action

- Recognize that trace metal accumulations in the ecosystem, both aquatic and terrestrial is a concern.

- Identify metals of interest and establish short and long-term strategies for dealing with the problems (e.g. prioritize metal problems but factor in a time frame for reassessment of priorities).

- Assess potential natural sources for metals in the environment. Determine relative importance of anthropogenic versus natural. Determining the natural or background signal could be used as the base line for studies in the future assessment of environmental degradation.

- Investigate the role of selected ecosystems as environmental sinks or sources for toxic metals (e.g., wetlands and volatilization of Hg from soils, respectively).

- Determine the "state" of the Michigan ecosystems with respect to toxic metals and identify potential CTB "hot spots."

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APPENDIX II

FOREST HEALTH MONITORING

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FOREST HEALTH MONITORING

FIELD METHODS GUIDE

(National Guide)

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U.S. Forest Service Laboratory
Research Triangle Park, NC 27709

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Environmental Monitoring and Assessment Program (EMAP)
U.S. Environmental Protection Agency
Office of Research and Development
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APPENDIX III

TRACE METALS RELATIVE RISK TASK FORCE MEMBERSHIP ROSTER

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