

**ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT**

**PROPOSED
NATIONWIDE HEAVY METALS POLLUTION
CONTROL PROGRAM**

**PREPARED BY
DIVISION OF FIELD INVESTIGATIONS - DENVER CENTER**

DENVER, COLORADO

AUGUST 1971



Metals Pollution Control
Program

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CONTENTS

Section	Page
INTRODUCTION	1
SUMMARY	3
THE PROBLEM	6
PRINCIPAL ELEMENTS OF CONCERN	6
Arsenic (As)	6
Copper (Cu)	6
Cadmium (Cd)	7
Lead (Pb)	7
Zinc (Zn)	7
Chromium (Cr)	7
Mercury (Hg)	7
Other Metals	7
THE OCCURRENCE OF HEAVY METALS IN THE AQUATIC ENVIRONMENT	8
The Polluting Mechanism	8
Natural Sources	9
Sources Attributable to Man's Activities	10
AVAILABLE INFORMATION ON HEAVY METALS POLLUTION	10
PROPOSED PROGRAM	16
OBJECTIVES	16
APPROACH AND PLAN OF PROGRAM	18
Screening Phase	18
Effluent Evaluation Phase	22
Intensive Evaluation Phase	23
Abatement Actions Phase	24
Technical Assistance and Follow-up Phase	24
ANALYTICAL SUPPORT	25
Limits of Detection	26
Availability of Instruction in EPA Facilities	28
Proposed Analytical Support	28

CONTENTS (continued)

	<u>Page</u>
BUDGET AND STAFFING	30
STAFF REQUIREMENT - FIELD INVESTIGATION CENTERS	30
STAFF REQUIREMENT - REGIONS	30
BUDGET	33

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page</u>
1	AREAS FROM WHICH RUNOFF MAY CONTAIN HEAVY METALS	Follows Page 9
2	SCHEDULE OF PHASES NATIONWIDE HEAVY METALS SURVEY	Follows Page 32

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
1	Classes of Industries and the Metals Which May Be Wasted	11
2	Comparison of Minimum Detection Limits by Wet Chemistry, Atomic Absorption Spectrophotometry and Atomic Fluor- escence Spectrophotometry	27
3	Staffing Requirements FY 72-74 Nationwide Heavy Metals Pollution Control Program	31

INTRODUCTION

The recent alarm created by discovery of hazardous concentrations of mercury in the nation's waterways, and the cleanup effort which followed, served to illustrate the many ways in which heavy metals and toxic substances can be introduced into man's environment, the insidious nature of such occurrences, and the utter lack of adequate safeguards against the resultant ecological effects. The focus of attention to the mercury scare, by all concerned with environmental protection, eclipsed the threat posed by other heavy metals and toxic substances. With the most apparent aspects of the mercury hazard now documented and subjected to the corrective processes, it is necessary that the Environmental Protection Agency turn its attention to the toxic elements and compounds which pollute the environment. Additionally, a more detailed follow-up examination of the mercury pollution situation is needed in order to identify and abate the less obvious sources. This plan proposes an approach to the orderly documentation of the pollution of the nation's waters by heavy metals and toxic substances and the means by which abatement would be attained.

The proposed program will be directed primarily toward the heavy metals Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Mercury (Hg), and Zinc (Zn), and the element Arsenic (As). Arsenic is not a metal, but the hazard to the environment, the biotic response, and the prevalence in industrial discharges require that this element and its derivative compounds be considered with the metals listed. The occurrence and

magnitude of pollution by other metals such as aluminum, iron, silver, selenium, molybdenum, uranium, and vanadium will be investigated where appropriate. For the sake of simplicity of presentation in this proposal, the terms "heavy metals" and "heavy metals and their salts" include the element arsenic and the derivatives of arsenic.

SUMMARY

With appropriate actions to correct the mercury pollution problem now under way, the Environmental Protection Agency must turn its attention to the equally great hazards associated with pollution by other heavy metals and toxic substances, and to the sources of such pollution. The elements, referred to herein as "heavy metals", which are of primary concern are Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Zinc (Zn) and Arsenic (As). The proposed study will also include analyses of all samples for Mercury (Hg). These elements are of particular significance because of their prevalence in natural runoff and industrial wastes, because of their toxic effect upon biota, and because of their persistence once introduced to the aquatic environment.

A nationwide heavy metals pollution control program is proposed.

The objectives and their priorities are:

1. Identify the waters in the nation which are polluted by heavy metals or for which there exists substantial threat of pollution.
2. Evaluate the actual and potential hazards associated with the polluted waters identified.
3. Identify the sources of heavy metals pollution and initiate their immediate abatement by the most expeditious means available.
4. Design and implement technical and administrative programs which will prevent recurrence of heavy metals pollution.

The proposed program would be carried out in five phases. The phases are of equal priority in that they are mutually supportive. All

phases are necessary to bring the program to a successful conclusion. The magnitude of several of the phases could be reduced, but only at the expense of adequate coverage.

Screening: A nationwide examination of heavy metals content in municipal and commercial water systems, irrigation waters and fisheries. The work will include review and updating of criteria for heavy metals in water, a review of existing heavy metals data, studies of geologic formations which yield heavy metals in runoff. From these findings, areas requiring more intensive examination would be identified.

Effluent Evaluation: An examination of industrial waste discharges to identify sources of heavy metals pollution.

Intensive Evaluation: Stream surveys in problem areas, as identified by the Screening Phase, to thoroughly evaluate the extent and magnitude of each problem area, to evaluate the effects on the receiving waters, and to develop the basis for appropriate abatement actions.

Abatement: Prepare abatement cases under the Refuse Act, the Water Quality Act, and new legislation, as appropriate.

Technical Assistance and Follow-up: Assist EPA Regional Offices in the establishment of monitoring and follow-up programs to insure prevention of future heavy metals pollution problems.

A nationwide program to be directed and supported by the Division of Field Investigations - Denver and Cincinnati Centers, is proposed. With new equipment now available, a viable program can be carried out in three years with the assignment of 32 positions to each of the Field Investigations Centers and 30 positions to the Regions. The three-year

cost, not including the Research Phase, is estimated at \$7,706,000.

The program, as proposed herein, is believed to be the minimum commitment and the optimum approach to a rigorous examination and abatement of heavy metals pollution of the nation's waters.

THE PROBLEM

PRINCIPAL ELEMENTS OF CONCERN

Seven "heavy metals" are of primary concern because of one or more of the following properties:

- Toxicity to living cells
- Tendency to accumulate in living tissues
- Concentrating effect in various food chains
- Solubility of metallic salts in water
- Persistence in water
- Synergisms
- Widespread occurrence

The seven metals and their effects are discussed briefly below. A more detailed discussion of the water quality significance of these metals is provided in Appendix A.

Arsenic (As) In elemental form, arsenic is insoluble in water, but many of the arsenates are highly soluble. Arsenic occurs naturally in waters of the western United States, and as a result of mining and industrial activities. Arsenic is directly toxic to humans and is believed to be carcinogenic.

Copper (Cu) Metallic copper is insoluble in water, but many salts of copper are highly soluble. Undesirable concentrations of copper are usually the result of corrosion of copper pipes, industrial discharges, and other activities of man. The primary significance of copper is its toxicity to aquatic organisms. Such toxicity is intensified by synergisms with other metals.

Cadmium (Cd) The chloride, nitrate, and sulfate of this metal are highly soluble. Cases of cadmium poisoning in humans are reported with increasing frequency, particularly in highly industrialized areas. Cadmium is concentrated in the liver, kidneys, pancreas, and thyroid of humans and other mammals.

Lead (Pb) Lead occurs as a result of natural and man-made conditions. It is a cumulative poison and, in soft water, is very toxic to humans.

Zinc (Zn) Salts of zinc, which are highly soluble in water, are often found in industrial wastes and in mine drainage. The significance of zinc as a water pollutant lies principally in the aesthetic effect of its milky appearance in water, in the taste imparted to drinking water, and in its toxicity to fish and aquatic organisms.

Chromium (Cr) Many of the salts of chromium are soluble in water and occur almost exclusively as a result of industrial discharges and treatment of cooling water. The hexavalent salts cause adverse physiological effects in humans and are cumulative in fish.

Mercury (Hg) Elemental mercury is insoluble in water, but is converted to methyl mercury by industrial and biological processes. In the methylated form, mercury is taken up by aquatic life and is concentrated through the food chain. The symptoms and effects of mercury poisoning in humans are well known.

Other Metals Although emphasis is placed upon the criticality of the seven "heavy metals" listed, others are believed to be of concern in certain areas. These include selenium (Se), molybdenum (Mo), vanadium (V), uranium (U), silver (Ag), and iron (Fe).

THE OCCURRENCE OF HEAVY METALS IN THE AQUATIC ENVIRONMENT

The Polluting Mechanism

Heavy metals are introduced to streams as a result of natural processes, man's activities, and combinations thereof. Most metals occur, in nature, as sulfides which are oxidized when exposed. This mechanism prevails both in the natural runoff situation and in mine drainage. The products of oxidation are sulfuric acid and solutions of metallic ions. The ions of some metals, such as lead and silver, combine with chlorides in water to form relatively insoluble products. Similarly, barium reacts with sulfate ions in water and precipitates.

Ferric iron adsorbs on silica, forming the characteristic "yellow boy" stain on rocky stream beds. These precipitates can limit or eliminate productivity in streams and are devastating to the aesthetic values of the affected waterway. These conditions are particularly prevalent in the eastern U.S. Under favorable pH and temperature conditions, other metals precipitate and become available for uptake by benthic organisms, or are redissolved after conversion to other forms. The other metals which remain in solution, in streams and impoundments, are available for uptake by aquatic plants and animals and can be concentrated through the food chain. Dissolved metals are also consumed directly by humans and higher animals, and are thus a health hazard. Mercury is the only metal known to be transported in elemental form by water. Heavy metals are introduced to the nation's waterways by a wide variety of industrial process waste discharges.

Natural Sources

Heavy metals are present, in trace quantities, in most of the rocks which form the earth's crust. Some areas or formations contain greatly more concentrated deposits. Such areas are usually associated with Tertiary or Recent volcanism. In the continental United States, most of these areas are located west of the Mississippi River. Exceptions include the Franklin Furnace area of New Jersey and the Driftless area of Wisconsin and Illinois. The latter contain base-metal sulfide deposits.

The tri-state district of Oklahoma, Kansas and Missouri is characterized by lead-zinc sulfides in bedded limestone. Other major metallic deposits are in the Basin and Range Province of Nevada, along the Rocky Mountains, and in the Cascade Range of Oregon and Washington. Locations of these areas are shown in Figure 1.

Areas in which streams are known to be polluted by runoff containing heavy metals include: the Tri-State area of Kansas, Oklahoma, and Missouri, the San Juan Mountains of southwestern Colorado, the Terlingua district of West Texas, the Coeur d'Alene district of Idaho, the Redding, California area, the Virginia City area of Nevada and California, and the Butte area of Montana. It is likely, even certain, that streams in many other areas are similarly affected.

Many groundwater bodies contain excessive amounts of metallic salts. Much work is needed to more clearly delineate such areas, and the possibilities for control of groundwater pollution sources require examination.



Figure 1. Areas From Which Runoff May Contain Heavy Metals

Sources Attributable to Man's Activities

Mining of metallic ores invariably involves exposure of lower grade materials containing metallic sulfides to air and/or water so that the oxidation products become available for transport to streams. Mining of other minerals similarly exposes metallic sulfides in stripped areas and in waste piles. Recovery and refining processes generate large volumes of waste liquors containing dissolved metals, which frequently find their way into surface and subsurface waters. Thus, the metals industries are frequently sources of heavy metals pollution.

A wide variety of industries use heavy metals and their salts as raw products or as process additives in ways which result in the generation of wastes containing the metals. Other industries remove metals and their salts as impurities and must dispose of these wastes in some way. Unfortunately, much of this material is ultimately transported to the nation's waters.

Classes of industries, and the metals which may be discharged as wastes, are summarized in Table 1. The industries listed are found in all parts of the continental United States, Alaska, Hawaii and Puerto Rico. Thus, the potential for heavy metals pollution is present throughout the United States and its possessions.

AVAILABLE INFORMATION ON HEAVY METALS POLLUTION

The body of knowledge regarding the occurrence of heavy metals pollution is grossly inadequate for analysis of the problem. The inadequacy of existing information is a function of limited recognition

TABLE 1.--Classes of Industries and the Metals Which may be Wasted

Industry	Metals
1. Electroplating	Copper, zinc, nickel, chromium, cadmium, lead, tin, aluminum, magnesium
2. Iron and steel pickling	Iron
3. Motor vehicles and parts	Chromium, iron, aluminum, zinc
4. Blast furnaces and steel mills	Iron, chromium, zinc, tin
5. Industrial gases	Chromium, iron, nickel, zinc
6. Ceramic	Iron, antimony, lead, aluminum, chromium, titanium
7. Cement	Aluminum, iron
8. Glass	Lead, aluminum, arsenic, variety of metallic oxides
9. Chlorine	Mercury
10. Electrothermal	Iron
11. Phosphorus	Iron
12. Nitrogen	Iron, aluminum
13. Bromine	Iron
14. Fluorocarbons	Antimony
15. Photographic products	Silver
16. Surface coating agents and pigments	Cobalt, manganese, lead, zinc, aluminum, chromium, titanium
17. Leather, gelatin, adhesives	Chromium
18. Agricultural chemicals	Copper, mercury, arsenic
19. Fragrance, flavor and food additives	Chromium, aluminum (catalysts)

Table 1 (Continued)

20. Oils, fats and waxes	Nickel
21. Soaps and detergents, fatty acids	Aluminum, zinc, magnesium, calcium
22. Pulp and paper	Aluminum, titanium
23. Plastics	Iron, lead, copper, aluminum (powdered metals as fillers), mercury, cobalt, silver
24. Man-made fibers and film	Manganese, cobalt, titanium, copper, palladium
25. Rubber	Aluminum, copper, zinc, chromium
26. Petroleum refining, petrochemicals	Lead, zinc, aluminum, cobalt, nickel
27. Intermediates, dyes	Iron, aluminum, copper, chromium, zinc, lead, sodium
28. Pharmaceuticals	Zinc, platinum, palladium, copper

of the importance of heavy metals in the aquatic environment, the dynamics of the problem within any given reach of stream, and the lack of accuracy and sensitivity (until recently) of data which have been acquired.

The National Water Quality Network (PHS-DWSPC) which evolved into the Water Pollution Surveillance System (FWPCA) gathered heavy metals data from some 130 stations throughout the nation. A summary of metals concentrations for Water Years 1962 through 1967 was recently published by the FWQA Division of Pollution Surveillance. These analyses show that 177 samples exceeded criteria established by the National Technical Advisory Committee for heavy metals. This report is a sophisticated and authentic analysis of the data, but the density of coverage of the nation's waters was probably less than one percent of that which is required for a rigorous evaluation of the problem.

The U. S. Geological Survey recently completed a "Reconnaissance of Selected Minor Elements in Surface Waters of the United States". The heavy metals content of "more than 720 water samples from urban and rural locations in all 50 states. . ." was compared to the mandatory maximum limits prescribed by the Public Health Service Drinking Water Standards. The limiting concentrations were exceeded, for one or more elements, in 45 samples. This reconnaissance provided useful, up-to-date information, but falls greatly short of the density of coverage needed. Moreover, samples were taken during low streamflow periods in order to minimize in-stream dilution. This approach does not provide for coverage of inputs from intermittent streams. The importance of

metals contributions by intermittent streams and sources will be discussed later.

Many random or short-term bits of heavy metals pollution data have been acquired by various agencies. Some of these data are available in published form and from STORET, but the majority are of limited value. Substantial strides have been made, in the very recent past, in analytical methods for the metals of concern, most notably Cd, Cr, Cu, Zn, and Hg. Much of the literature and stored data reflect earlier metals data obtained by less sensitive and precise analyses than are now available, and results are reported accordingly. Many of the present standards and criteria are based upon those questionable data. Moreover, recent studies show that lower concentrations of heavy metals are significant in terms of the aquatic environment.

The chemistry and dynamics of heavy metals in water are such that minor changes in temperature and alkalinity can cause precipitation, ion exchange, or chemical combinations within relatively short reaches of streams. This fact makes it necessary that a comprehensive evaluation of heavy metals pollution, within a given watershed, be based upon a density of sampling locations which will insure coverage of all sources as well as all important water uses. The literature cited above falls far short of such coverage in all of the geographic locations which must be surveyed. Although better examples doubtless exist in the highly industrialized areas of the eastern and southern United States, the following two areas in Colorado illustrate the point:

1. Headwaters streams of the Colorado River Basin such as the Eagle River and Roaring Fork are known to contain

concentrations of heavy metals which are hazardous to the aquatic environment or to humans. Communities in Colorado such as Minturn, Rifle, Red Cliff, DeBeque, and Eagle obtain domestic water supplies from the headwaters streams and from the Upper Colorado River. Numerous diversions for agricultural use (irrigation and stock watering) are located throughout the Basin.

The most upstream sampling point considered in the studies cited above was at Fruita, which is located well downstream from some of these points of use. The data, thus, shed no light on the suitability of these streams for the uses to which the waters are subjected.

2. Clear Creek, which is known to be polluted by mine drainage throughout most of its length, is the water supply for Thornton, Westminster, Silver Plume, Starkville, Golden, and Arvada, as well as a major source for the Consolidated Mutual Water Company of the Denver metropolitan area. There is no information in the USGS or WPSS studies regarding the heavy metals content of Clear Creek.

In summary, there is virtually no information available which is of suitable accuracy and density to form the basis for a nationwide evaluation of the heavy metals pollution situation. That which is available will be carefully examined and, where appropriate, will be incorporated into the studies proposed herein.

PROPOSED PROGRAM

The Field Investigations Centers - Denver and Cincinnati - are charged with ". . . . emergency response on a nationwide basis concerning pollution of the water environment", and to "conduct complex field investigations requiring specialized interdisciplinary competencies". The proposed program, thus, is clearly of the form and substance contemplated in the functional statements for the Centers.

The Denver Center laboratory is rapidly approaching operational status and, by the target date for initiation of this proposed program, will be capable of supporting the study in the western U. S. The Cincinnati Center is partially equipped to support the program in the eastern U. S. Purchase of some additional equipment will be necessary. With modest augmentation of the engineering and specialty staffs, the Centers can provide the direction, coordination, data processing and analysis, and report production required. The Headquarters Research staff should be assigned responsibility for a timely review of the applicable heavy metals criteria and standards. It will be necessary to assign a full-time heavy metals program coordinator in each Regional Office for the duration of the program.

OBJECTIVES

A many-faceted program is required to evaluate the extent and magnitude of the heavy metals pollution problem, to update the criteria especially in terms of domestic consumption; to abate the pollution sources; and to provide the basis for prevention of heavy metals

pollution in the future. The objectives are to:

1. Identify the waters in the nation which are polluted by heavy metals or for which substantial threat of pollution by heavy metals exists.
2. Evaluate the actual and potential hazards associated with the polluted waters identified.
3. Identify the sources of heavy metals pollution and initiate their immediate abatement by the most expeditious means available.
4. Assist Regional staffs with the design and implementation of technical and administrative programs which will prevent recurrence of heavy metals pollution.

APPROACH AND PLAN OF PROGRAM

Screening Phase

The screening operation is designed to carry out the tasks which are necessary to identify reaches of streams, impoundments, and ground water bodies which are polluted by heavy metals. These tasks include the establishment of "sorting limits", a review of existing heavy metals data, a study of geologic formations to identify areas from which runoff could be expected to contain heavy metals, and analysis of water samples from points of significant* water use. These tasks are described below.

Standards and criteria for certain of the heavy metals are expressed in narrative terms or in terms of bioassay results. These criteria vary widely (see Appendix A) and require translation to numerical criteria for use in the screening operation. The DFI staffs will review existing criteria and recent research findings, and derive numerical criteria based, where possible, upon solid technical evidence. In the absence of such evidence "sorting limits" based upon the best information available will be established. Such criteria leave much to be desired from a technical and scientific standpoint. Their use in this program will be limited to the flagging of those waters and effluents requiring further study in the Intensive Evaluation Phase.

As indicated earlier, existing heavy metals data from all appropriate sources will be utilized to the extent possible. In view of recent advances in analytical technique and data reporting, highly selective sorting of existing data will be required. Data, which by virtue of analytical and reporting techniques employed are of suitable

* Points of significant water use are defined as municipal water systems, commercial water systems serving 100 or more persons, and major irrigation diversions and fisheries.

quality, will become input to the Screening Phase.

Primary sources of existing data will be the STORET system and the state water pollution control agencies. State Fish and Game agencies will be asked to furnish information regarding waters in which heavy metals pollution affects fisheries. Heavy metals data in the STORET system will be sorted against the numerical limits which are to be established during the Research Phase. Data made available by state agencies will be stored by the Denver and Cincinnati Centers and sorted similarly.

A review of the mineralogy of outcrops which affect surface water quality, and of formations which determine the metals content of major groundwater supplies, will be conducted to identify streams and water supplies which should be sampled in the Screening Phase. This review will also identify waters which can be expected to contain significant concentrations of metals other than the seven principal elements for which analyses are to be performed on all samples.

Both surface and groundwater domestic supplies are to be evaluated in the screening operation. Samples from water systems will be subjected to analysis for the seven principal elements plus those indicated by the mineralogic review as being significant in each case. In addition to the seven principal elements, samples from the major irrigation diversions will be analyzed for the metals which are critical in terms of plant uptake, such as boron and molybdenum. Similarly, samples from established fisheries will be analyzed for the metals which are critical to fish and the food chain as well as those which are concentrated in fish flesh.

The Geological Survey measured heavy metals concentrations during low-stream flow periods, during the Reconnaissance of Minor Elements, based upon the assumption that maximum metals concentrations would occur when the least quantity of dilution water was present in streams. This assumption is only partially correct. In semi-arid and arid regions (which coincide, generally, with the areas of Tertiary and Recent volcanism mentioned earlier) many headwaters streams are dry at times during which main streams are at low-flow. These headwaters streams are primary sources of naturally occurring heavy metals pollution. Thus, contributions of metals may be at a lower-than-average level or non-existent during the low-flow period. A more extreme situation is illustrated by the Bagdad Copper Mine in Arizona, and the Kennecott Mine and Mill, Tyrone, New Mexico, in which metals-laden wastes are discharged to intermittent streams. During much of the year, these wastes percolate into the dry streambeds, such that they are subject to leaching and flushing into higher order streams during runoff periods. In such areas sampling should be scheduled during low-flow periods and during periods when tributaries are flowing. Another consideration is that natural alkalinity, which promotes precipitation of some metals, is usually at highest levels during low flow. Additionally, "low-flow" is not a consideration in reaches downstream of impoundments in which current patterns are such that mixing occurs, or if "plug flow" prevails. Most reservoirs are characterized by one of these two possibilities. In short, it will be necessary to study each basin carefully and schedule sampling accordingly.

There are some 20,000 water systems in the United States and territories. It is estimated that upwards of one-fourth of these will require sampling more than once during the Screening Phase. Adding the supplementary sampling of irrigation diversions and fisheries, the total number of samples to be generated by the Screening Phase may reach 25,000.

The Regional Heavy Metals Program Coordinators would have as a primary task during the Screening Phase, the coordination of sampling by water system personnel, irrigation district personnel, and state and local water pollution control staffs. Samples would be analyzed at DFI laboratories. In view of the logistics and the many samples involved, no attempt would be made to provide the custody accorded samples and data which are to be used in abatement proceedings. The data would be evaluated to locate problem areas and sources. The Critical Evaluation phase is designed to provide more intensive sampling in the problem areas. The sampling and associated analysis and data handling would be carried out under appropriate custodial controls.

The Screening Phase can be completed in approximately 18 months with the commitment of resources recommended in the Budget and Staffing portion of this proposal. The water sampling program will be carried out by state and local officials, water and sewage treatment plant operators, etc., under the guidance and supervision of the Regional Coordinators. It is estimated that 24 man-months of effort will be required by the Regional Coordinators to carry out the coordination of this phase. The review of existing data, the mineralogy review, the establishment of numerical criteria, the analyses of samples, and evaluation of data

will be conducted by the DFI staffs. The DFI manpower requirement for completion of this phase is expected to be 680 man-months.

Effluent Evaluation Phase

A review of industrial waste inventories, indices such as Dunn & Bradstreet, will be carried out to identify industries of the types listed in Table 1. Information obtained from the National Industrial Inventory and Refuse Act permit applications will be integrated into the study. Liquid effluents from industries identified will be analyzed for heavy metals content. If discharge is to a municipal collection and treatment system, the municipal waste will be sampled at the point of discharge and will be similarly analyzed. Sampling of industries identified by the review process can begin shortly after initiation of the review, and should provide the basis for large numbers of Refuse Act cases.

It is anticipated that additional industrial sources will be identified as a result of the screening operation. These will be sampled as they become evident. Thus the Effluent Evaluation Phase cannot be completed prior to completion of the Screening Phase. Effluent samples from industries so identified will be analyzed for the seven principal elements, plus those of water pollution significance which are associated with the particular industry. Full custodial control of effluent samples will be maintained.

The review of industrial waste source information will be carried out jointly by the Regional Coordinators and the DFI staffs. Collection and analysis of industrial waste samples will be conducted by the DFI staffs.

This phase is expected to generate about 10,000 samples and will require commitment of 34 man-months by the Regional Program Coordinators and 550 man-months by the DFI staffs.

Intensive Evaluation Phase

The Intensive Evaluation Phase is designed as the follow-up to the Screening Phase. Streams, impoundments, and groundwater supplies which are identified by the screening operation as having excessive concentrations of metals will be examined closely to determine the extent and magnitude of the problem, to identify the sources, and to assess damage to the waters. This examination will include analysis of aquatic organisms, fish, and sediment for heavy metals. In the case of polluted groundwater supplies, the causes or sources of the pollution will be identified by DFI specialists and appropriate control measures will be recommended.

This activity may generate upwards of 10,000 water, effluent, fish, benthos, and sediment samples. Full custodial control must be maintained upon each sample and the analytical data. Regional Coordinators and staffs will be called upon to obtain and compile existing data, make initial investigations, and carry out local coordination. DFI-Denver and Cincinnati crews will conduct the stream surveys and effluent evaluations. Work can begin on this phase shortly after initial results from the screening and effluent sampling become available, but cannot be considered complete until the last samples from the other phases have been analyzed. The manpower requirements can be expected to amount to 30 man-months by the Regional Coordinators and staffs and 738 man-months by the Denver and Cincinnati Field Investigations staffs.

Abatement Actions Phase

As indicated earlier, Refuse Act cases should be generated almost from the initiation of the Effluent Evaluation Phase. Information developed by the effluent and intensive sampling can be expected to provide the basis for substantial numbers of new or reconvened enforcement conferences. It is impossible to predict actual numbers of abatement actions which will grow out of the Heavy Metals Program, but the total will probably be of such numbers that additional staff will be required at the Headquarters level to provide timely handling of the cases.

The DFI staffs can be expected to devote approximately 272 man-months during this phase to the preparation of reports and supporting materials for the abatement actions. The Regional Coordinators will commit 30 man-months. This activity is expected to continue indefinitely with commitment of 36 man-months per year by the Centers and 12 man-months per year by the Regional Coordinators.

Technical Assistance and Follow-up Phase

The abatement actions resulting from the Heavy Metals program will require a substantial follow-up effort. The primary activity in this phase will be the resampling and reevaluation of effluents and reaches of streams to insure that abatement schedules are met. It will, moreover, be necessary that the Regions utilize the findings of the Heavy Metals Program to design new surveillance schemes and augment existing systems such that recurrence of heavy metals pollution will be discerned immediately.

This activity will be carried out locally by the Regional Heavy Metals Program Coordinators with technical and laboratory backup from the DFI Centers.

It is expected to require 5 man-months of effort by Coordinators, and 60 man-months by DFI personnel. This activity is expected to continue indefinitely and will require commitment of 36 man-months per year by the Centers and 12 man-months per year by the Regional Coordinators.

ANALYTICAL SUPPORT

A variety of analytical methods are available for heavy metals in water. Virtually all metals can be quantified by standard colorimetric or "wet chemical" methods. Most of these procedures have been supplanted by more accurate (and often faster) instrumental methods, but wet chemistry is the best method, at this time, for arsenic, selenium, vanadium, and boron. Arsenic can be determined most accurately by the Silver Diethyldithio-carbamate Method. Selenium requires the Diaminobenzidine Method. Vanadium can be analyzed by the Catalytic Oxidation Method. Analysis for boron requires the Dianthrime method. All of these procedures are described in recent issues of Standard Methods.

Fortunately, most metals can be detected with relative ease by atomic absorption spectrophotometry (AA). Samples of industrial effluents and many natural waters may be aspirated directly into the flame with satisfactory accuracy. Lower detection limits can be obtained by chelation and extraction with methyl isobutyl ketone (MIBK) or by evaporation. Maximum production capacity for cadmium, zinc, copper, lead and chromium is about 40 samples per day.

Other methods which are available for trace metal analysis include emission spectrophotometry, spark source mass spectrometry,

atomic fluorescence, and neutron activation.

Emission spectrophotometry can be used to detect many metals, simultaneously, in a sample. Sensitivity depends upon the salt concentration in a sample and is often inferior to that of the AA. Furthermore, the instrumentation is expensive (\$80 - \$90,000). A spark source mass spectrometer can measure all of the elements simultaneously in a sample. Sensitivity is generally inferior to other methods, and though a sample can be analyzed in 20 minutes, without computer, as much as an entire day of the analyst's time may be required to calculate the results. Price of the instrument, without computer, is about \$100,000.

Atomic Fluorescence Spectrophotometry (AFS) offers production advantages in heavy metals analysis, but the instrument has not been shown to be of sufficient accuracy for the work contemplated. An automated unit costing approximately \$42,000 is now being produced by Technicon Instrument Company. This instrument is capable of analyzing up to 100 samples per hour, for six elements including copper, cadmium, chromium, and zinc. It is expected that this capability will soon include arsenic, lead, and selenium. In the event accuracy and sensitivity are improved to acceptable levels, consideration will be given to the employment of AFS equipment.

Neutron activation can often produce highly accurate results, but is of no value for production analyses of large numbers of samples.

Suitable production rates of mercury analysis can be attained by automating the Coleman instruments now in use.

TABLE 2

Minimum Detection Limits by
Wet Chemistry and Atomic Absorption Spectrophotometry

<u>Element</u>	<u>Wet Chemistry ($\mu\text{g/l}$)</u>	<u>Atomic Absorption ($\mu\text{g/l}$)</u> <u>Direct Chelate Extraction</u>	
Aluminum (Al)	50		
Arsenic (As)	1		
Barium (Ba)		100	
Beryllium (Be)		10	
Boron (B)		20	
Cadmium (Cd)		1	< 1
Chromium (Cr)		10	1
Cobalt (Co)			1
Copper (Cu)		5	1
Iron (Fe)			
Lead (Pb)		10	1.0
Lithium (Li)		5	
Manganese (Mn)		5	1
Molybdenum (Mo)	1		
Nickel (Ni)			1
Selenium (Se)	1		
Silver (Ag)		10	1
Strontium (Sr)		10	
Vanadium (V)	0.1		
Zinc (Zn)		5	

Limits of Detection

Minimum detection limits by wet chemistry and AA are listed in Table 2. The limits are considered to be satisfactory for the work proposed. There is need, however, for an instrumental method for arsenic analyses. All possible avenues leading toward an acceptable instrumental method will be explored prior to and during the Heavy Metals program.

Availability of Instrumentation in EPA Facilities

Present capabilities for production analyses of heavy metals samples are summarized below:

1. DFI-Cincinnati - Three AA's are committed to mercury analyses.
2. AQC, Cincinnati - One AA and one emission spectrograph, which could provide limited support.
3. Kerr laboratory, Ada - Two AA's and one ommission spectro-photometer, all of which are being used on technical support projects in the South Central Region (Region VI); limited manpower available.
4. Corvallis laboratory - Two AA's, one with computer printout, working almost continuously on regional surveillance needs.
5. Southwest Region (Region IX), Alameda laboratory - Two AA's doing surveillance work.
6. Southeast laboratory, Athens - Two AA's primarily committed to oil analyses. A spark source mass spectrometer without computer printout has recently been obtained.
7. DFI-Denver Center - One AA which must be available for other DFI-DC studies.

As is evident, an attempt to accomplish a viable heavy metals survey with existing equipment would bring virtually all other analytical support activities to a standstill.

Proposed Analytical Support

Most of the considerations cited herein weigh heavily in favor of production analyses using the Atomic Absorption Spectrophotometer and automated mercury analysis units of the type now in use, at central locations. This concept is most efficient in terms of laboratory manpower and capital investment, and permits centralized data handling and evaluation. The Instrumentation Laboratories (IL) Model 353 Atomic Absorption Spectrophotometer is a proven workhorse in many water quality laboratories and will be utilized for most of the production analyses. Two each with automated sampling equipment and digital printout will be required by each laboratory. Specialized analyses will be carried out using a Jarrel-Ash Quantometer. This instrument will provide the capability of analyzing a wide variety of elements in a single scan. With this equipment the DFI laboratories, with staffs of twelve, will be able to provide the production analyses required to support the nationwide program.

BUDGET AND STAFFING

STAFF REQUIREMENT - FIELD INVESTIGATION CENTERS

A technical, scientific, and clerical staff of 32 will be required for each Field Investigation Center. Position classifications are listed in Table 3. The staffs will provide direction, technical assistance, and laboratory support to the Nationwide Heavy Metals Pollution Control Program. Additional specialty functions will be performed, as required, by DFI personnel now assigned. Recruitment of the staff should be initiated at once, with a target completion date of January 1, 1972. Completion of the staff by that date will permit accomplishment of the planning, reconnaissance, and training which is necessary if field work is to begin in early 1972.

STAFF REQUIREMENT - REGIONS

A staff of 3 technical, and clerical personnel will be required in each EPA Region to carry out the tasks outlined herein. Position classifications are listed in Table 3. The distribution of positions and classifications is based upon present knowledge of the nature and magnitude of the heavy metals pollution problem and may require adjustment as the program proceeds. The main thrust of the Heavy Metals Program should be completed by the end of FY 74. A one-man staff should remain in each Region thereafter, as indicated in Figure 2. Staff requirements for the Research Phase are to be determined by the Office of Research and Monitoring and are not included herein.

TABLE 3

Staffing Requirements FY 72-74^{1/}
 Nationwide Heavy Metals Pollution Control Program

Division of Field Investigations - Denver Center^{2/}

Program Director - Physical Science Administrator	GS-14
Chemical, Sanitary or Industrial Engineer (5)	GS-11-12-13
Mining or Geological Engineer (2)	GS-12
Hydrologist (2)	GS-11-12-13
Programmer - Analyst	GS-12
Chemist	GS-12
Chemist (3)	GS-11
Chemist (4)	GS-9
Aide (2)	GS-5-7
Engineering Technician (6)	GS-5-7
Secretary-Steno (2)	GS-5
Clerk-Typist (3)	GS-4
Total - 32 positions	

Division of Field Investigations - Cincinnati Center^{2/}

Program Director - Physical Science Administrator	GS-14
Chemical, Sanitary or Industrial Engineer (5)	GS-11-12-13
Mining or Geological Engineer (2)	GS-12
Hydrologist (2)	GS-11-12-13
Programmer - Analyst	GS-12

^{1/} Assumes availability of Atomic Fluorescence Spectrophotometry by December 1, 1971

^{2/} Requirements listed are in Addition to staff presently assigned

TABLE 3 (Continued)

Chemist	GS-12
Chemist (3)	GS-11
Chemist (4)	GS-9
Aide (2)	GS-5-7
Engineering Technician (6)	GS-5-7
Secretary-Steno (2)	GS-5
Clerk-Typist (3)	GS-4
Total - 32 positions	

Each EPA Regional Office

Survey Coordinator	GS-14
Sanitary, Chemical or Industrial Engineer	GS-11-13
Sec'y Steno	GS-4-5
Total - 30 positions	

Figure 2

SCHEDULE OF PHASES
NATIONWIDE HEAVY METALS SURVEY
ENVIRONMENTAL PROTECTION AGENCY

Division of Field Investigations
Denver - Cincinnati

April 1971

Phase	FY - 72	FY - 73	FY - 74	Beyond FY - 75
Screening	500 14	180 10		
Effluent Evaluation	90 10	230 12	230 12	
Intensive Evaluation	140 8	258 8	340 14	
Abatement Actions	38 4	100 6	138 5	36/yr 12/yr
Technical Assistance and Follow-up			60 5	36/yr 12/yr
<p>KEY <u>man-months DFI</u> man-months Regions</p>				

BUDGET

Costs of the Heavy Metals Pollution Control Program are tabulated below, by fiscal year and by organization. Personnel costs are based upon Step 3 of each grade, 8 1/2 percent for benefits, and a 5 percent cost of living increase annually and 10 percent for administrative overhead.

<u>DFI-DC</u>	<u>FY 72</u> <u>(\$1000)</u>	<u>FY 73</u> <u>(\$1000)</u>	<u>FY 74</u> <u>(\$1000)</u>
Personnel	455	562	722
Travel	240	240	240
Equipment	98	12	12
Reagents & Supplies	<u>4</u>	<u>4</u>	<u>4</u>
YEARLY TOTALS	797	818	978

Total FY 72-74 = \$2,593,000

<u>DFI-CC</u>	<u>FY 72</u> <u>(\$1000)</u>	<u>FY 73</u> <u>(\$1000)</u>	<u>FY 74</u> <u>(\$1000)</u>
Personnel	455	562	722
Travel	240	240	240
Equipment	98	12	12
Reagents & Supplies	<u>4</u>	<u>4</u>	<u>4</u>
YEARLY TOTALS	797	818	978

Total FY 72-74 = \$2,593,000

<u>Regions</u>	<u>FY 72</u> <u>(\$1000)</u>	<u>FY 73</u> <u>(\$1000)</u>	<u>FY 74</u> <u>(\$1000)</u>
Personnel	54	67	86
Travel	10	10	10
Equipment & Supplies	<u>5</u>	<u>5</u>	<u>5</u>
Annual Budget - each Region	69	82	101

Total FY 72-74 = \$2,520,000

<u>Estimated Total Costs</u>	<u>FY 72</u> <u>(\$1000)</u>	<u>FY 73</u> <u>(\$1000)</u>	<u>FY 74</u> <u>(\$1000)</u>
Total Program Costs per year	2,284	2,456	2,966
Total - FY 72-74 = \$7,706,000			

APPENDIX A

WATER QUALITY SIGNIFICANCE OF VARIOUS HEAVY METALS

APPENDIX A

Introduction

The material presented in this appendix is taken from a technical report (TR-2) entitled "The Impact of Various Metals on the Aquatic Environment", authored by Mr. Robert F. Schneider and published by the Division of Field Investigations - Denver Center. Information on mercury was researched by Mr. Michael R. Helton. Messrs. Schneider and Helton are respectively Chief, Biology Section and Staff Engineer, DFI-DC.

WATER QUALITY SIGNIFICANCE OF VARIOUS HEAVY METALSArsenic (As)

Water Quality--Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. In its elemental form, arsenic is insoluble in water, but many of the arsenates are highly soluble. Most, if not all, natural waters contain arsenic compounds. Its natural occurrence is very common in the freshwater of the western United States. Elsewhere (i.e., New Zealand) lethal doses of arsenic (20 mg/animal lb.) have been recorded as occurring naturally in freshwater.

Through domestic water supplies, arsenic compounds are constantly taken into the human body where they are cumulative. Human blood normally contains 0.2 to 1.0 mg/l of arsenic.

In seawater, normal arsenic concentrations are recorded to be 0.003 mg/l. As mentioned above, arsenic compounds are cumulative in living tissue. Thus, in the sea, marine plants (i.e., brown algae)

have been found to contain concentrations up to 30 mg/k. Arsenic is also commonly found in marine animals. According to the work of Vinogradov, it accumulates up to 0.3 mg/k in some molluscs, coelenterates, and crustaceans. McKee and Wolf report that shellfish may contain over 100 mg/kg.

Biotic Response--Arsenic is notorious for its toxicity to humans. Ingestion of as little as 100 mg usually results in severe poisoning and as little as 130 mg has proved fatal. Several incidents have demonstrated that arsenic in water may be carcinogenic. Cancer of the skin and possibly of the liver are attributed to arsenic in drinking water.

Some bioassay work has been done with arsenic, but the results are not based on standard testing methods such as the 96-hour TL_m . It is interesting to note that arsenic concentrations of 3-20 mg/l have not harmed aquatic insects such as immature dragonflies, damselflies, and mayflies. Rudolfs also reported that concentrations of 2-4 mg/l of arsenic did not interfere in any way with the self-purification of streams.

Standards--Governmental water quality codes often briefly define hazardous metals and for abatement purposes the common code statement is ". . . no toxic materials (metals, often understood) in concentrations that will impair the usefulness of receiving waters as a source of supply or interfere with other legitimate use of said water". Limits for arsenic in water, as suggested by various agencies, are summarized in Table I which follows.

TABLE 1.--Arsenic (As) Concentration (mg/l)

Arsenic Concentration	Organization & Date of Recommendation	Comment
0.05	USPHS, 1942	Maximum permissible concentration in drinking water.
0.05	USPHS, 1946	Maximum permissible concentration in drinking water.
0.2	W.H.O., 1958	Maximum allowable concentrations for potable water.
0.2	W.H.O. European, 1961	Tolerance limit for drinking water standards.
0.05	USPHS, 1962	Maximum allowable limit for drinking water.
0.1	USPHS, 1962	Recommended limit for drinking water.
0.05	State of California, 1963	Maximum limit for domestic water supplies.
1.0	State of California, 1963	Maximum limit for irrigation water supplies.
1.0	State of California, 1963	Maximum limit for stock and wildlife watering.
1.0	State of California, 1963	Maximum limit for fish and other aquatic life waters.
0.05	State of Texas, 1967	Maximum limit for inland waters.
1.0	State of Texas, 1967	Maximum limit for tidal waters.
0.05	State of Colorado (date unknown)	Maximum allowable limit for surface waters to be used for public water supply - after complete treatment.
0.05	State of Florida (date unknown)	Maximum allowable limit for surface waters in Florida.
0.05	State of Illinois (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Indiana (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Iowa (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.

TABLE 1.--Arsenic (As) Concentration (mg/l)--Continued

Arsenic Concentration	Organization & Date of Recommendation	Comment
0.01	State of Minnesota (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Mississippi (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Alaska (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Connecticut (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Maine (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Michigan (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Montana (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Nevada (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Ohio (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Rhode Island (date unknown)	Same as USPHS, 1962, standards for drinking water.
0.05	State of Vermont (date unknown)	Same as USPHS, 1962, standards for drinking water.

Copper (Cu)

Water Quality--Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. High concentrations of cupric ions are not likely to be found in natural surface or groundwaters. This is because as they are introduced into natural waters of pH7 or above, these ions quickly precipitate and are thereby removed by adsorption and/or sedimentation.

In natural freshwater, copper salts occur in trace amounts, up to about 0.05 mg/l. In seawater, copper is found at a level of 0.003 mg/l. Therefore, the presence of greater amounts of copper salts is generally the result of pollution, attributable to the corrosive action of the water on copper pipes, to industrial discharges, or frequently to the use of copper compounds for the control of undesirable algae.

Copper is not considered to be a cumulative systemic poison, like lead or mercury. In humans, most of the copper ingested is excreted by the body and little is retained. In lower organisms there is some record of accumulation. Marine animals have been found to contain 4 to 50 mg/l and in some sponges accumulation has exceeded these values.

Biotic Response--In concentrations high enough to be dangerous to humans, copper renders a disagreeable taste to the water. Threshold concentrations for taste have been reported in the range of 1.0 - 2.0 mg/l of copper, while 5.0 - 7.5 mg/l makes the water completely undrinkable. For this reason it is believed that copper is seldom a hazard to domestic supplies.

Copper is present in trace amounts in all living organisms. It is believed to be essential for nutrition.

The toxicity of copper to aquatic organisms varies significantly not only with the species, but also with the physical and chemical characteristics of the water (e.g., temperature, hardness, turbidity, and carbon dioxide content). Concentrations, toxic to a variety of aquatic organisms, may vary from 0.015 to 3.0 mg/l depending upon the water chemistry.

Copper acts synergistically with the sulfates of other metals such as zinc and cadmium to produce a potent toxic effect on fish. Synergism also exists between copper and mercury.

Standards--Limits set for copper in water vary markedly. Table 2 summarizes recommendations established by various agencies.

Cadmium (Cd)

Water Quality--The elemental form of cadmium is insoluble in water, although the chloride, nitrate, and sulfate of this metal are highly soluble. In the literature reviewed, no "normal" level for freshwater was recorded. Mention was made of "normal" levels for seawater of < 0.08 mg/l.

Cadmium salts may be found in wastes from electroplating plants, pigment works, textile printing, lead mines, and certain chemical industries. Lieber and Welsch reported groundwater contamination by cadmium to the extent of 3.2 mg/l on Long Island, N.Y., as the result of an electroplating industry's waste discharge. High concentrations

TABLE 2.--Copper (Cu) Concentration (mg/l)

Copper Concentration	Organization & Date of Recommendation	Comment
0.02	USPHS, 1925	Mandatory maximum limit for drinking water.
3.0	USPHS, 1942	Recommended limit for drinking water (not mandatory).
3.0	USPHS, 1946	Recommended limit for drinking water (not mandatory).
3.0	State of Oklahoma, 1957	Limit for municipal water supply.
0.2	State of Oklahoma, 1957	Limit for agricultural water use.
1.0	State of Oklahoma, 1957	Limit for recreational waters.
1.0	W.H.O., 1958	Permissible limit for drinking water.
1.5	W.H.O., 1958	Excessive limit for drinking water.
3.0	W.H.O. European, 1961	Limit after 16 hours contact with new pipe, but distribution system should have < 0.05 mg/l copper.
1.0	USPHS, 1962	Recommended limit for drinking water.
1.0	State of California, 1963	Threshold concentration in domestic supplies.
0.1	State of California, 1963	Threshold concentration in irrigation supplies.
0.02	State of California, 1963	Threshold concentration for fresh-water fish and aquatic life.
0.05	State of California, 1963	Threshold concentration for sea-water fish and aquatic life.
1.0	State of Texas, 1967	Recommended limit for inland and tidal waters.
-	FWPCA, 1968	Water Quality Criteria for aquatic life. Maximum copper concentration any any time or place should not be greater than 1/10 the 96-hour TL_m value, nor should any 24-hour average concentration exceed 1/30 of the 96-hour TL_m value.
1.0	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

TABLE 2.--Copper (Cu) Concentration (mg/l)--Continued

Copper Concentration	Organization & Date of Recommendation	Comment
1.0	State of Connecticut (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.5	State of Florida (date unknown)	Maximum allowable limits for surface waters to be used for drinking water shellfish, fish and wildlife, and industrial water supply.
1.0	State of Illinois (date unknown)	Maximum allowable for drinking water.
1.0	State of Maine (date unknown)	Maximum allowable for drinking water.
1.0	State of Michigan (date unknown)	Same as USPHS 1962 Drinking Water Standards.
1.0	State of Minnesota (date unknown)	Maximum allowable limit for drinking water.
0.2	State of Minnesota (date unknown)	Maximum allowable limit for recreation water, fish propagation and wildlife.
1.0	State of Montana (date unknown)	Same as USPHS 1962 Drinking Water Standards.
1.0	State of Nevada (date unknown)	Same as USPHS 1962 Drinking Water Standards.
1.0	State of Rhode Island (date unknown)	Same as USPHS 1962 Drinking Water Standards.
1.0	State of Vermont (date unknown)	Same as USPHS 1962 Drinking Water Standards.

of cadmium have been reported in Missouri mine waters. One spring in the area had 1,000 mg/l of cadmium.

Biotic Response--Cadmium is moderately toxic to all organisms and it is a cumulative poison in mammals. It tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans and other mammals.

Common levels found in marine plants are approximately 0.4 mg/l, while in marine animals a range of 0.15 to 3 mg/l has been recorded.

Few studies have been made of the toxicity of cadmium in the aquatic environment. Medical reports are of little value because the adverse effects of human ingestion vary appreciably from person to person.

Aquatic organisms (i.e., Daphnia magna) are currently being exposed to cadmium and other toxic metals via bioassay techniques at the National Water Quality Laboratory, Duluth, Minnesota, laboratories. Preliminary results indicate Daphnia are very sensitive to cadmium; the LD-50 (3 wk.) was 5 mg/l in Lake Superior water. Other unpublished data reveal no effect to fathead minnows or bluegills exposed to 37 µg/l through a complete generation. The tests also indicate that following prolonged exposure there is a large accumulation of cadmium in fish.

Cadmium acts synergistically with zinc to increase toxicity. Hublou, Wood, and Jeffries found that cadmium concentrations of 0.03 mg/l in combination with 0.15 mg/l of zinc from galvanized screens caused mortality of salmon fry.

Standards--Standards and criteria for cadmium in water are summarized in Table 3.

Lead (Pb)

Water Quality--Some natural waters contain lead in solution, as much as 0.8 mg/l. These concentrations are most often found in mountain streams flowing through mineralized areas. Surface and groundwaters used for drinking supply in the United States often have a trace of lead but it seldom exceeds 0.04 mg/l.

The lead concentration in seawater is about 0.00003 mg/l. It is found in marine plants at a level of 8.4 mg/l. Residues in marine animals reach a concentration in the range of 0.5 mg/k. Lead is highest in calcareous tissue. Higher concentrations than listed above are usually the result of pollution from mines or leaded gasolines.

Biotic Response

Lead tends to be deposited in bone as a cumulative poison. Sensitivity to lead poisoning differs with individuals, as concentrations causing human sickness may vary from 0.042 to 1.0 mg/l. Lead has an antagonistic effect with calcium. In soft water, lead may be very toxic at concentrations of 0.1 mg/l. In hard water, these concentrations are not toxic. The Ohio River Valley Water Sanitation Commission reported that calcium in a concentration of 50 mg/l completely destroyed the toxic effect of 1.0 mg/l of lead.

Standards--Standards and criteria for lead content in water are summarized in Table 4.

TABLE 3.--Cadmium (Cd) Concentrations (mg/l)

Cadmium Concentration	Organization & Date of Recommendation	Comment
0.1	USSR, 1949	Maximum permissible concentration in domestic supplies of Russia.
0.0	State of Oklahoma, 1957	Suggested criteria for municipal, industrial, agricultural, recreation, fish and wildlife water use.
0.05	W.H.O. European, 1961	Maximum tolerance limit for drinking water.
0.01	USPHS, 1962	Maximum allowable limit for drinking water.
0.02	State of Texas, 1967	Maximum limit for inland and tidal waters.
-	FWPCA	The concentration of cadmium must not exceed 1/30 of the 96-hour TL_m concentration at any time or place and the maximum 24-hour average concentration should not exceed 1/500 of the 96-hour TL_m concentration.
0.01	State of Alaska (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.01	State of Colorado (date unknown)	Maximum allowable limits for drinking water.
0.01	State of Connecticut (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.01	State of Illinois (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Illinois (date unknown)	Maximum allowable limit for fish propagation and wildlife waters.
0.01	State of Indiana (date unknown)	Maximum allowable limit for drinking water.
0.01	State of Iowa (date unknown)	Maximum allowable limit for drinking water.
0.01	State of Maine (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.01	State of Michigan (date unknown)	Same as USPHA 1962 Drinking Water Standards.
0.01	State of Minnesota (date unknown)	Maximum allowable limit for drinking water.

TABLE 3.--Cadmium (Cd) Concentrations (mg/l)--Continued

Cadmium Concentrations	Organization & Date of Recommendation	Comment
0.01	State of Mississippi (date unknown)	Maximum allowable limit for drinking water.
0.01	State of Montana (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.01	State of Nevada (date unknown)	Same as USPHS 1962 Drinking Standards.
0.01	State of Ohio (date unknown)	Maximum allowable limit for drinking water.
0.01	State of Rhode Island (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.01	State of Vermont (date unknown)	Same as USPHS 1962 Drinking Water Standards.

TABLE 4.--Lead (Pb) Concentrations (mg/l)

Lead Concentration	Organization & Date of Recommendation	Comment
0.1	USPHS, 1925	Maximum permissible concentration in drinking water.
0.3	Germany, 1933	Temporary concentration in drinking water that had been in pipes for 24 hours.
0.1	USPHS, 1942	Maximum permissible concentration in drinking water.
0.1	USPHS, 1946	Maximum permissible concentration in drinking water.
0.02	Uruguay, 1951	Maximum recommended limit in potable water.
0.3	Netherlands, 1953	Temporary concentration in drinking water that had been in pipes for 24 hours.
1.0	Mersey and Severn River Boards in England (date unknown)	Working standards for all heavy metals in certain English streams.
0.1	W.H.O. International, 1958	Maximum allowable limits for lead in drinking water.
0.1	International Water Supply Association (USA, Great Britain, France, and Netherlands), 1958	Maximum allowable limits for lead in drinking water.
0.1	W.H.O. European, 1961	Maximum tolerance limit for drinking water.
0.05	USPHS, 1962	Maximum allowable limit for drinking water.
0.1	State of California, 1963	Maximum limit for surface waters used by fish or to be processed for human consumption.
0.1	State of Texas, 1967	Maximum limit for inland waters.
0.5	State of Texas, 1967	Maximum limit for tidal waters.
0.05	FWQA, 1970	Physiologically safe in water for lifetime.
2-4	FWQA, 1970	Physiologically safe in water for period of a few weeks (borderline health hazard thereafter).

TABLE 4.--Lead (Pb) Concentrations (mg/l)--Continued

Lead Concentration	Organization & Date of Recommendation	Comment
8-10	FWQA, 1970	Toxic in water with exposure of several weeks.
>15	FWQA, 1970	Lethal, unknown concentration probably more than 15 mg/l for a period of several weeks.
0.05	State of Alaska (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.05	State of Colorado (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Connecticut (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.05	State of Florida (date unknown)	Maximum allowable limit for drinking water, industrial supply, agriculture, fish propagation and wildlife, and recreation.
0.05	State of Illinois (date unknown)	Maximum allowable limit for drinking water.
0.1	State of Illinois (date unknown)	Maximum allowable limit for fish propagation and wildlife waters.
0.05	State of Indiana (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Iowa (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Maine (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.05	State of Minnesota (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Mississippi (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Nevada (date unknown)	Same as USPHS 1962 Drinking Water Standards.
0.05	State of Ohio (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Rhode Island	Same as USPHS 1962 Drinking Water Standards.
0.05	State of Vermont (date unknown)	Same as USPHS 1962 Drinking Water Standards.

Zinc (Zn)

Water Quality--Some zinc salts (e.g., zinc chloride and zinc sulfate) are highly soluble in water. These salts are often found in industrial wastewater from galvanizing industries, and manufacturers of paint pigments, cosmetics, pharmaceuticals, dyes, insecticides, and numerous other products. In zinc-mining areas, this metal has been found in natural waters in concentrations as high as 50 mg/l.

In most freshwater (surface and ground), zinc is present only in trace amounts. Some evidence has been presented which indicates that zinc ions are absorbed strongly and permanently on silt, with the resultant inactivation of the metal.

In seawater, the normal zinc concentration is about 0.01 mg/l. Marine plants may contain up to 150 mg/l of zinc, while marine animals contain ranges of 6 to 1,500 mg/l.

High concentrations of zinc in domestic water are undesirable from an aesthetic standpoint as well as from a health hazard standpoint. At a concentration of 30 mg/l, zinc gives water a milky appearance. Concentrations as low as 5.0 mg/l cause a greasy film on boiling of the water. The soluble salts of zinc impart an unpleasant, astringent taste to water and can be detected in concentrations as low as 4.3 mg/l.

Biotic Response--Zinc has no known adverse physiological effects upon man except at very high concentrations (i.e., 675-2,280 mg/l causes vomiting). In fact, zinc is an essential and beneficial element in human nutrition. Normal uptake by humans is 10-15 mg/day.

Zinc exhibits its greatest toxicity toward fish and aquatic organisms. In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/l have been reported to be lethal, but calcium is antagonistic toward such toxicity.

Fish sensitivity to zinc varies with species, age and condition of the fish, as well as the physical and chemical characteristics of the water. Bioassay results are listed in detail by McKee and Wolf.

There is some controversy as to a synergistic effect between zinc and copper. Doudoroff and Katz believe a synergistic effect exists, while the Water Pollution Research Board of England disagrees. The key to this disagreement appears to be the hardness of the water, but more study will be required before a definite statement can be made.

Standards--Zinc "taste tests" have been partly instrumental in changing the standards for potable supply. This is one reason for the range in limits listed in Table 5.

Chromium (Cr)

Water Quality--The Chromic (trivalent) salts of chloride, nitrate, and sulfate, and the hexavalent chromate and dichromate salts of ammonia, potassium, and sodium are all water soluble. Other chromium salts are insoluble. Concentrations of chromium range from 0 to 2.3 mg/l in surface waters, and chromium concentrations of about 1.5 mg/l may impart color and taste to water.

TABLE 5.--Zinc (Zn) Concentrations (mg/l)

Zinc Concentrations	Organization & Date of Recommendation	Comment
5.0	USPHS, 1925	Maximum permissible concentration in drinking water.
15.0	USPHS, 1942	Recommended limited concentration in drinking water.
15.0	USPHS, 1946	Recommended limited concentration in drinking water.
1.0	Mersey and Severn River Boards in England, 1953	Working standards in English streams for all heavy metals in combination with zinc.
5.0	W.H.O. International, 1953	Permissible limit in drinking water.
15.0	W.H.O. International, 1958	Excessive limit in drinking water.
5.0	W.H.O. European, 1961	Recommended limit for drinking water.
5.0	USPHS, 1962	Recommended limit for drinking water.
5.0	State of Texas, 1967	Maximum limit for inland and tidal waters.
5.0	State of Alaska (date unknown)	Same as USPHS 1962 Drinking Water Standards.
5.0	State of Connecticut (date unknown)	Same as USPHS 1962 Drinking Water Standards.
1.0	State of Florida (date unknown)	Maximum allowable limit for drinking water, industrial supply, agriculture, fish and wildlife, and recreation.
5.0	State of Illinois (date unknown)	Maximum allowable limit for drinking water.
1.0	State of Illinois (date unknown)	Maximum allowable limit for fish and wildlife waters.
5.0	State of Maine (date unknown)	Same as USPHS 1962 Drinking Water Standards.
5.0	State of Michigan (date unknown)	Same as USPHS 1962 Drinking Water Standards.
5.0	State of Minnesota (date unknown)	Maximum allowable limit in drinking water.
5.0	State of Montana (date unknown)	Same as USPHS 1962 Drinking Water Standards.

TABLE 5.--Zinc (Zn) Concentrations (mg/l)--Continued

Zinc Concentration	Organization & Date of Recommendation	Comment
5.0	State of Nevada (date unknown)	Same as USPHS 1962 Drinking Water Standards.
5.0	State of Rhode Island (date unknown)	Same as USPHS 1962 Drinking Water Standards.
5.0	State of Vermont (date unknown)	Same as USPHS 1962 Drinking Water Standards.

Hexavalent chromium salts may be found in wastes discharged from electroplating plants, tanneries, chromium treated cooling waters, and plants which manufacture paints, dyes, explosives, ceramics, paper, and many other substances. Trivalent chromium salts are less widely used and are not considered toxic to man; these salts have not been extensively considered in water quality studies.

Biotic Response--Chromium is not an essential element in the nutrition of humans or aquatic animals. Ingestion of large doses of chromate by man may cause corrosion of the intestine and nephritis; however, it appears that humans can safely drink water containing 5.0 mg/l of hexavalent chromium. Although hexavalent chromium is rapidly eliminated from the human body, there is evidence of a pronounced cumulative toxicity to salmon and rainbow trout exposed to sublethal concentrations. The toxicity of chromium to aquatic life varies widely, and is influenced by temperature, pH, the chromium valence, synergism, and antagonism (hardness is especially antagonistic), dissolved oxygen concentration, and the species involved.

Data presented by McKee and Wolf lead to the conclusion that fish are relatively tolerant of chromium (most of the 96-hour TL_m values ranging from about 100 to about 135 mg/l), while lower forms of aquatic life are very sensitive to chromium. Daphnia magna exhibited toxicity thresholds ranging from 0.016 to 0.7 mg/l. The concentrations of chromium that inhibit algal growth have been reported by FWPCA to range 0.032 to 6.4 mg/l; sublethal concentrations sometimes stimulate algal growth.

On the basis of a large amount of information reviewed, McKee and Wolf suggested that 1.0 mg/l chromium (trivalent or hexavalent) would not interfere with fish life, and that 0.05 mg/l would not interfere with other aquatic life.

Standards--The maximum concentration of 0.5 mg/l of chromium recommended for water supplies by the U. S. Public Health Service in 1946 (and consequently by many other water quality agencies) was based on the minimum concentration of chromium detectable at that time; today, much lower concentrations are detectable. A limit of 0.05 mg/l seems unnecessarily stringent for the protection of human health; however, maximum concentrations of 0.05 mg chromium per liter are reasonable for the protection of aquatic life.

A summary of limits for chromium concentrations in water, as recommended by various agencies, is included in Table 6, which follows.

Mercury (Hg)

Water Quality--Elemental mercury is insoluble in water and has heretofore been presumed non-toxic to biota and of little concern as a pollutant. However, recent investigation has exposed a process of mercury methylation in the environment by bacteria that causes a transformation of the relatively nontoxic elemental mercury to toxic methyl mercury, which is capable of concentration by living organisms. Recently, the disasters of the 1953 Minamata Bay, Japan, mercury poisoning were brought to the attention of the United States public by the poisoning of a New Mexico family (in a way totally unrelated to the process of the Minamata Bay event) by eating pork contaminated by

TABLE 6.--Chromium (Cr) Concentrations (mg/l)

Chromium Concentration	Organization & Date of Recommendation	Comment
None	USPHS, 1942	No hexavalent Cr permissible in drinking water.
0.05	USPHS, 1946	Hexavalent; maximum permissible in drinking water.
1.0	Severn and Mersey River Boards, England, 1953	Working standard for all heavy metals in combination (including Cr).
0.05	W.H.O. International, 1958	Hexavalent; drinking water.
0.05	W.H.O. European, 1961	Hexavalent; drinking water.
0.05	USPHS, 1962	Hexavalent; drinking water.
0.05	State of California, 1963	Either valency; drinking water.
5.0	State of California, 1963	Either valency; stock and wild-life watering.
1.0	State of California, 1963	Either valency; fish propagation.
0.05	State of California, 1963	Either valency; protection of other aquatic life.
"caution"	FWPCA, 1968	"Water Quality Criteria" - urged caution in discharge of chromium.
0.05	USPHS, 1969	Hexavalent; drinking water.
0.05	ORSANCO, 1970	"Standard 1-70," hexavalent; <u>or</u> shall not harm aquatic life to a degree of 1/20 96-hour TL _m .
0.05	U.S. Army (date unknown)	Hexavalent; Ammunition Procurement and Supply Agency Regulation No. 11-11 (subject to revision).

being fed on a seed treated with an organic mercury compound.

In the aquatic environment, elemental mercury may be converted to methyl mercury by the above-mentioned biological methylation process, or the methyl mercury may be discharged by any one of a large number of industrial processes using mercury, such as chlor-alkali, acetylene, polyvinylchloride, fungicide, batteries, papermaking and paint manufacturing. Total domestic use of mercury for 1969 was about 6 million pounds, with various amounts of the total reputed lost to the environment; one value presented to the Senate subcommittee investigating mercury pollution of the environment was 1,200,000 pounds lost per year.

Mercury is found naturally in sea water at a level of 0.00003 mg/l and in sea plants at approximately 0.03 mg/l. Canadian pickerel taken from the Great Lakes have contained concentrations of mercury as high as 5 parts per million, while walleye pike have been found to contain mercury in concentrations as high as 1.40 to 3.57 parts per million. Abelson indicates that the concentration factor of mercury from water is on the order of 3,000 or more, while Klein and Goldberg report that mercury levels in coastal marine organisms are several orders of magnitude greater than comparable volumes of sea water. Higher volumes of mercury are found in sediments near sewer outfalls, as compared to similar deposits further removed. While testifying before the Senate Subcommittee on Energy, Natural Resources and the Environment, Klein further speculated that the concentration factor of methyl mercury from water to fish was at least 1 million.

Biotic Response--Mercury ions are considered to be toxic to various forms of aquatic life. For the stickelback, the lethal concentration has been found to range in the area of 0.008 mg/l, while the effect on phytoplankton of a concentration of 0.06 mg/l of ethyl mercury phosphate was found to be lethal. Other researchers have reported that 0.5 mg/l of mercury added as mercuric chloride resulted in a 50 percent inactivation of photosynthesis of the giant kelp. Corner and Sparrow report that the toxic effects of mercury salts are accentuated by the presence of trace amounts of copper.

Methyl mercury in humans is reported to penetrate the brain membrane, causing wide disintegration of brain cells. The appearance of symptoms of mercury poisoning may be delayed for as long as several months. When the symptoms do appear, they may not be specific but may include fatigue, numbness of the extremities, difficulty in swallowing, deafness, blurring of vision, loss of muscular coordination, slurring of speech and impairment of hearing. The symptoms are described as the behavior of the Mad Hatter, a reference to the occupational disease of felt workers, exposed to mercury used in shaping felt.

Standards--At the time of the first public concern regarding mercury contamination of environmental media in this country, no domestic standards were in force that attempted to place a limit on the concentration of mercury in water. Additionally, the World Health Organization also had no available limits on mercury. An interim standard for mercury was adopted from the U.S.S.R., where a value of 0.05 mg/l had been imposed on water. Subsequently, the Food and Drug Adminis-

tration placed a limit on the concentration of mercury in food shipped in interstate commerce at 5 parts per million. The Severn and Mersey River Boards in England have as a working standard, a limit of total concentration of heavy metals, including mercury, of one (1.0) milligram per liter.

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