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Technical and Microeconomic Analysis Arsenic and Its Compounds

Versar, Inc.

Prepared For
Environmental Protection Agency

April 1976

EPA 560/6-76-016

TECHNICAL AND MICROECONOMIC ANALYSIS

TASK III – ARSENIC AND ITS COMPOUNDS

APRIL 12, 1976

FINAL REPORT

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

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The intentional production and use of arsenic and its compounds is greatly exceeded by the quantities unintentionally mobilized by industrial activities. The arsenic currently in food and water presents no identifiable health hazard, and the present controls on arsenical products, by a number of Government agencies, appear adequate. Emissions to the air from high-temperature processes are large, particulate collection devices appear largely inadequate, and the dangers presented are of serious concern.

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For

U. S. Environmental Protection Agency
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REVIEW NOTICE

This report has been reviewed by the Office of Toxic Substances, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Con't)

TABLE OF CONTENTS (Con't)

Page

LIST OF TABLES

LIST OF TABLES (Con't)

LIST OF FIGURES

Page

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Appreciation is extended to the many individuals who participated in this effort. The organizations cooperating were:

Government Agencies

- Department of Agriculture, Agricultural Research Service
- Environmental Protection Agency, Office of Pesticide Programs
- Food and Drug Administration
- Department of Interior, Bureau of Mines
- Department of Labor, Occupational Safety and Health Administration

Trade Associations

- American Wood-Preservers' Association, Washington, D.C.
- Lead Industries Association
- National Agricultural Chemical Association, Washington, D.C.
- National Cotton Council, Memphis, Tenn.
- National Paint and Coatings Association, Washington, D.C.

Private Companies

- Abbott Laboratories, North Chicago, Ill.
- American Smelting and Refining Co., New York, N.Y.
- Ansul Co., Marinette, Wisc.
- Battelle Laboratories, Columbus, Ohio
- Buckman Laboratories, Inc., Memphis, Tenn.
- Chevron Chemical Co., Richmond, Cal.
- W.A. Cleary Corp., New Brunswick, N.J.
- Commercial Chemical Co., Memphis, Tenn.
- C.P. Chemicals, Inc., Sewaren, N.J.
- E.S.B., Inc., Philadelphia, Pa.
- Fleming Laboratories, Inc., Charlotte, N.C.
- Koppers Co., Inc., Pittsburgh, Pa.
- Los Angeles Chemical Co., South Gate, Cal.
- Pennwalt Co., Bryan, Texas
- Salsbury Laboratories, Charles City, Iowa
- Thompson-Hayward Chemical Co., Kansas City, Kansas
- Ventron Corp., Beverly, Mass.
- Voluntary Purchasing Group, Bonham, Texas

SECTION I

INTRODUCTION

Objectives of the Study

Efforts by various parts of the U.S. Environmental Protection Agency, EPA contractors, other Government agencies and other workers in the field are making increasingly apparent the present and potential dangers to man and the environment from unrestricted production and use of certain toxic chemical substances. For many of these substances, there is ample evidence that the substances are in fact toxic. However, these substances have, in general, beneficial uses and are of value to the private and public sectors of the U.S. economy. Hence, the posture of the EPA with respect to these substances is neither a blanket endorsement of current and projected practices as presenting no real danger; nor is it, at the other extreme, a total and immediate ban of the production and use of these substances. Realistically, for many of these toxic substances, a careful assessment is required of the dangers and of the options reasonably available for reducing the dangers.

This report is the partial result of a study specifically intended to provide such objective data for several toxic chemical substances. The substances covered in this report are elemental arsenic and arsenic compounds.

The specific objectives of this study of arsenic (and its compounds) are:

1. To objectively and quantitatively evaluate the real dangers (both present and projected to man and to the environment, without the implementation of new and specific control measures.
2. To make an accounting of how, where, and how much arsenic is entering the environment in accessible (and possibly dangerous) forms.
3. To identify control alternatives which may be technologically and economically feasible, and to evaluate the effectiveness of each of these control alternatives in reducing the overall danger of arsenic to man and the environment.

4. To delineate the present and projected role of arsenic (and its compounds) in the U.S. economy, and to evaluate the impact of each of the control alternatives upon the economy.

Previous Studies of Arsenic

Much has already been published on the various aspects of arsenic and the environment. Various investigators over the years have separately reported on the physical, chemical and biological properties of arsenic and its compounds; on the natural abundance and polluted levels found in air, water, and food; on the toxicology and estimated human dose rate ranges; and on the movement and effects of arsenic in the ecosystem. Much less has been reported on the unintentional mobilization of arsenic (as an impurity) by industry; on the flow of arsenic in society (i.e., in the economy); on the potential for substitutes in commercial applications; on the identification of pollution sources and of abatement practices; and on the costs of abatement and of use restrictions.

Study of these aspects of arsenic and the environment have been severely hampered by the fact that no authoritative U.S. production or consumption data have been published since 1959, when the American Smelting and Refining Company (ASARCO) became the sole U.S. producer of white arsenic. The U.S. Bureau of Mines has since then withheld these data to protect the proprietary interests of ASARCO.

Arsenic as a minor constituent of industrial wastewaters and of industrial land-destined wastes has received much less attention than the heavy metals in the many recent EPA studies on an industry-by-industry basis for effluent guidelines development and for hazardous waste practices. A possible explanation is that while atomic absorption is a rapid and economical analytical technique for the determination of heavy metals, it requires more modification of technique and matrix correction for arsenic determination so that alternate separate and specific methods are usually preferred when the determination of arsenic is mandated.

There have been several recent publications which cover more than a narrow aspect of the subject of arsenic and the environment. Among these are the publications of Sullivan,(2) Davis,(9) Whitacre and Pearse,(30) and Wood.(42) However, these were for the most part still addressed to only a portion of the subject, and none were intended to be a comprehensive and detailed encyclopedia for arsenic.

Scope of This Study and Report

In light of what already has been published and what has not, this study and report attempts to provide a resource analysis for arsenic and its compounds with as complete a breadth of coverage as was practicable within time and budgetary constraints. It was felt that an appreciation of all aspects of the commercial and environmental flow of arsenic was needed to realistically assess any dangers and to formulate and assess options for reducing the dangers.

This resource analysis of arsenic may be divided into four major subjects. First is a detailed review of the occurrence and chemistry (Section III and of the toxicology (Section VI) of arsenic and its compounds. These are the areas which have received considerable attention from other investigators but which, to our knowledge, have not been assembled before in a comprehensive fashion suitable for achieving the objectives of this study. Included in Section IV are natural occurrence, chemistry of the element, analytical determination and coprecipitation, white arsenic refining, chemistry in fresh water, chemistry in soils, removal from soils, plant uptake, biological transformation and the effects of phosphorus on arsenic transport. Section VI includes exposure standards, acute and chronic effects, levels in foods and in tissues, modes of toxicological action, oxidation state vs. toxicity, organic vs. inorganic arsenicals, and the metabolism of arsenical animal feed additives.

The second major subject of this report systematically covers, for the first time (to our knowledge), the many commercial raw materials, processes, and products in which arsenic and its compounds are involved as an impurity or byproduct. A stated intent of this effort (in Section V and in part of Section VIII) was to quantify the commercial mobilization of arsenic. In a few cases, adequate data were found to generate rather precise estimates. In many other cases, the estimates were made to the best of our judgement despite a lack of consistent or verified data; the entry "no available data" purposefully was never used. Our intent in going on record with estimates was frankly to invite controversy, hopefully to solicit constructive criticism of these estimates which should eventually lead to a set of data with a much-improved confidence level. Section V includes, for each commercial occurrence of arsenic, the quantified fate of this arsenic through our economy and especially into our environment. Section VIII treats the potential for the commercial occurrences of arsenic becoming sources for commercial arsenic.

The third major subject of this resource analysis of arsenic is the intentional commercial flow of arsenic and its compounds (as opposed to the unintentional flow of Section V). This subject, in Section IV and in Section VIII, is usually based, for other commodities, upon comprehensive historical data gathered and published by the Bureau of Mines and by the Bureau of the Census. In the case of arsenic, however, such data has not been published for the past 16 years, in order to protect the interests of ASARCO, the sole U.S. producer of white arsenic. Hence, quantifying the intentional commercial flow of arsenic was an exercise in detective work and in estimation. As in the "commercial mobilization" effort, estimates were always made; no entry was left blank or given such a wide span which would have made the matrix useless for the project objectives. We again invite criticism of our estimates. This analysis had one less degree of freedom, however: the independently-derived estimates of the total white arsenic supply and demand were made to balance each other. In addition to the quantification of the commercial flow of arsenic and its compounds, Sections IV and VIII discuss the quantities released to the environment at each step of processing, transfer, and use; the substitutes available in each use category, the price of each arsenical product relative to its arsenical ingredient and relative to its replacements, and the price elasticity of its demand (how its use would vary with the price of its arsenical starting material).

The fourth major subject in this report is an assessment of the first three subjects in relation to each other and in relation to the objectives of this project. Section VII assesses the health hazard (both present and projected) from arsenic and its compounds resulting from intentional and unintentional commercial mobilization, production, conversion, consumption, and disposal; without the implementation of new and specific control measures. Section IX presents and evaluates control alternatives for reducing the health hazard, and screens out those which are not needed, not feasible, not effective, or too costly on an a priori basis. Those control alternatives passing the screening process of Section IX are analyzed in Section X for their estimated impact upon the economy.

Constraints Upon This Study and Report

As alluded to before, this investigation proceeded without access to the specific white arsenic production and consumption data as gathered by the Bureau of Mines, the Bureau of the Census, or other Government agencies.

This investigation did not have the time, funds, or mandate to generate any new experimental data.

This study, and the conclusions and recommendations resulting from this study, was intended to assess the role of arsenic in the U.S. economy and in the general environment; i.e., the exposure of the general population to the overall environment. It was not intended to substitute for other Governmental activities in much more specific areas of interest. This study did not deal with arsenic regulations for the work environment, as this is the province of the Occupational Safety and Health Administration of the Department of Labor. This study did not deal with arsenic regulations which are the province of the Food and Drug Administration. This study only marginally touched upon the province of the Office of Pesticide Programs of the Environment Protection Agency, mainly because the major commercial use for arsenic is in pesticides; any appearance that this study was for the purpose of influencing pesticide registration is purely unintentional.

SECTION II

CONCLUSIONS

Societal Flow of Arsenic

The table on the succeeding page is a quantitative summary of where arsenic is found, produced, converted, used, and inadvertently altered. Of the arsenic in the commercial flow in the United States, this summary table presents estimates of the amounts dissipated in end products, of the amounts dissipated to land, and of the amounts accessible to the environment via air, water, and land discharges. The differentiation between the arsenic dissipated to land and the arsenic in land discharges is that the former means a general distribution over wide areas of the country, whereas the latter means a deposit of a waste material in a bounded (and relatively small) area specifically set aside for waste disposal.

This table contains no notations as to the confidence in the various estimates or to the consistency and extent of the data behind the various estimates. The reader is referred to the body of this report for the generation of the estimates.

The entries in this table are in terms of metric tons per year (1974 basis) of elemental arsenic. The actual chemical and physical forms of the quantities, the concentrations at which arsenic and its compounds exist for each entry, and the nature of the matrix in which these arsenical materials exist are discussed in the body of this report.

The results of this study are grouped into four broad categories. First are those dealing with the industrial sources of arsenic and the emissions and dissipations from these sources. The second group deals with the commerical flow of white arsenic and its derivatives. Third are the conclusions concerning the dangers presented to man and to the environment. Last are the control alternatives and their assessment in reducing these dangers.

SUMMARY OF U.S. ARSENIC FLOW, DISSIPATIONS, AND EMISSIONS
METRIC TONS PER YEAR (1974 BASIS)

	Commercial Receipts	Commercial Shipments	Dissipation in End Products	Dissipation to Land	Airborne Emissions	Waterborne Effluents	Land-Destined Wastes
Primary Zinc							
In Zn Concentrates	525						
Losses in Smelting					190	0.4	120
Residues to Pb Smelters		210					
Retained in Zn Products			5				
Primary Lead							
In Pb Concentrates	850						
In Residues from Zinc	210						
Losses in Smelting					240		800
Retained in Pb Products			20				
Primary Copper							
In Cu Concentrates	35,000						
Losses in Smelting					4,800	32	3,400
In Acid Leach Residues				8,800			
In Collected Flue Dusts		8,300					9,600
Retained in Cu Products			43				
Other Primary Non-Ferrous Metals							
In Ore Concentrates	150						
Losses in Smelting					50		50
For Pigments, etc.			50				
Lead Alloys							
Arsenic Imported for Alloying	580						
Reclaimed from Products	955						
Losses in Processing					130		300
Contained in Products Shipped			1,105				
Copper Alloys							
Arsenic Imported for Alloying	107						
Reclaimed from Products	75						
Contained in Products Shipped			182				
Phosphates							
In Consumed Phosphate Rock	555						
In Fertilizer				293			
In Animal Feed and Other Products			30	32			
In Detergents						110	
From Product Purification							90
Water and Wastewater Treatment							
Water Treatment Sludges				65			
Wastewater Treatment				2	1		
Borax and Boric Acid							
In Refined Borax	22						
Losses in Boric Acid Production						3.9	
Retained in Products			18				
Manganese Ore							
In Mn Ore Concentrates	4,000						
Losses in Smelting				1,080	10		350
In Ferroalloys to Iron & Steel		2,160					
In Batteries and Other Products			400				
Iron and Steel							
In Iron Ore	54,000						
In Ferroalloys	2,160						
Losses in Steelmaking				36,000	12		1,250
Retained in Steel Products			15,500				
Losses in Cast Iron Foundries					20		100
Retained in Cast Iron Products			3,300				
Coal							
In Coal	2,450						
Losses in Combustion					650		1,800
Petroleum							
In Petroleum	120						
Losses in Combustion					108		
In Non-Fuel Products			12				
White Arsenic Production & Conversion							
From Domestic Cu Flue Dusts	8,300						
Imported	8,550						
Pesticide Production		12,790			130		
Wood Preservative Production		1,400					
Food Additive Production		407			2		
Glass Additives		1,805					
Misc. Uses		320					
Use of White Arsenic & Derivatives							
Pesticides	12,790			10,490	2,300		
Wood Preservatives	1,400		1,400				
Food Additives	407			407			
Glass Manufacture	1,805		1,595		210		
Misc. Uses	320		320				
TOTALS	108,000 (Net)	-	23,900	57,170	8,850	150	17,860

Industrial Sources of Arsenic

1. The quantity of arsenic recovered for commercial sale from copper smelting is less than 25 percent of the arsenic estimated to be in the copper ore concentrates. Most of the remaining arsenic reports in slags, sludges, waste flue dusts, and acid plant residues, all eventually disposed of on land. Very little of the arsenic is discharged in wastewaters or is retained in refined copper products. However, it is estimated that 14 percent of the arsenic originally in the copper ore concentrates is emitted to the atmosphere; this quantity amounts to 4,800 metric tons per year and is more than all other sources of airborne arsenic emissions put together.

2. The historical basis for the large quantities of arsenic emitted to the air from copper smelters is related to the emissions of sulfur oxides. The practice in past years was that sulfur oxides capture (for sulfuric acid manufacture) was limited to converter flue gases, which contain two-thirds of the sulfur originally in the ore concentrate. The sulfur in the flue gases from the prior process steps of roasting and smelting was too dilute for economical recovery. However, the arsenic partition is exactly opposite: two-thirds of the arsenic is volatilized in the roasting and smelting operations. When flue gases are used to make sulfuric acid, cold-gas cleaning (wet scrubbing as well as dry dust collection) assures arsenic removal. When sulfur-bearing flue gases are emitted, dry dust collection techniques such as cyclones, "balloon flues", electrostatic precipitators, and baghouses are only partially effective in capturing arsenic (as explained below).

3. New emission standards for sulfur oxides from copper smelters, aimed at 90 percent overall capture of sulfur, are resulting in process changes such that considerably more of the arsenic

(and cadmium, lead, etc.) is being captured as well as sulfur.

4. In the primary copper industry, in other non-ferrous primary metals industries, and in coal combustion at electric power generation stations, one-third to one-half of the arsenic in flue gases escapes dry dust collection devices despite nominally-high particulate collection efficiencies for these devices. As_2O_3 does not condense below 295°C and then only slowly (the particle nucleation and growth processes are relatively slow). Conversely, electrostatic precipitators and baghouses are routinely kept above the dew point of the flue gases, electrostatic precipitators are run at elevated temperatures where the gas resistivities are more favorable, and collected flue dusts in the non-ferrous metals industries are commonly recycled, providing more opportunities for arsenic loss.
5. Airborne emissions of As_2O_3 from all sources amount to as much as the domestic commercial production of this material.
6. Except for the arsenic in phosphate detergents, and some small loss via wastewaters from copper smelters, the waterborne effluents of arsenic are virtually zero. The standard treatment of wastewaters containing arsenic and other metals is lime addition, with a flocculent such as ferric chloride, and sedimentation. In the non-ferrous metals industry, such treatment is required and justified for the removal of heavy metals; the cost of this treatment is not borne by the necessity to remove arsenic.
7. Much of the arsenic in commercial materials reports in land-destined industrial wastes. Much of this arsenic is in a relatively insoluble form, as complex arsenates in slags.

However, a substantial portion is subject to further mobilization via wind-dispersion of collected flue dusts, and via leaching and runoff of sludges. Sulfide sludges are particularly vulnerable to leaching.

8. Very little of the arsenic in non-ferrous metal ores and concentrates is retained in the refined non-ferrous metal products. The smelting and refining processes either vaporize the arsenic, remove it via a basic flux into a slag, or leave it in electrolysis residues.

9. Arsenic occurs as a minor constituent in a great many commercial crude materials at concentrations which are highly variable but which are commonly two to four orders of magnitude greater than the average crustal concentration of 2 to 5 ppm. Two types of such enriched minerals are prevalent: in sulfide ores such as copper, lead, zinc and other non-ferrous metal ores; and in sedimentary deposits where arsenic had been originally coprecipitated by hydrous iron oxide. Significant quantities of arsenic are found in such sedimentary materials as phosphate rock, borax, manganese ore, and iron ore. The concentrations of arsenic in iron ore, pig iron, and steel and cast iron products were estimated, but were not extensively verified. Because of the huge commercial quantities of ferrous metals, however, the quantities of arsenic are correspondingly huge. It is estimated that the arsenic in iron ore is more than that in all non-ferrous ores, and more than the total arsenic in all other commercial materials put together.

10. The arsenic in iron ore is retained through the blast furnace process as stable and non-volatile iron arsenides. Basic steelmaking processes remove the bulk of the arsenic as an arsenate. The huge quantity of steelmaking slags containing arsenic is used commercially for many purposes.

11. While the arsenic concentration in coal is about the average crustal concentration, the arsenic quantities mobilized are large because of the magnitude of the coal industry. This quantity is expected to grow dramatically. Phosphate rock is another growth industry where arsenic is involved.

12. Searles Lake brines contain large quantities of arsenic which conceivably could be recovered.

13. Three new technologies for energy production have important arsenic implications. Early data on coal gasification indicates that two-thirds of the arsenic is volatilized. Oil shale may mobilize more arsenic by 1990 than is presently mobilized by the copper and other non-ferrous metal industries. Geothermal energy development could also mobilize large quantities of arsenic.

14. Metallic arsenic is an alloying element for lead and copper in several important uses. Much of these arsenical nonferrous alloys are recovered, however, in the secondary metals industry; the arsenic in reclaimed metals is as much as the quantity of new arsenic used for alloying. There are significant losses, however, in the processing of reclaimed metals.

Commercial Flow of White Arsenic and Its Derivatives

1. It is estimated that the U.S. production of white arsenic is only 7 percent of the arsenic in all crude commercial materials, and that the total quantity of arsenic potentially available as a supply source should grow to be much larger in the near future. Much of the present and future arsenic resource should be recoverable by hydrometallurgical processes.

2. The potential supply of white arsenic, in the United States and world-wide, far exceeds the current or potential demand. Arsenic and its derivatives are consequently low-priced commodities.

3. The domestic production of white arsenic by the single manufacturer increases as both white arsenic price and domestic copper production increase, on a year-to-year basis. Both factors are of approximately equal importance in affecting the production level. It is expected, however, that several new and important factors are changing this relationship: the increase in copper ore leaching, the process changes brought about by tighter SO_x regulations upon copper smelters, and (most important) the proposed changes in OSHA standards. Alternate sources for arsenic supply also potentially exist.

4. Arsenical products compete directly with petrochemicals in most use categories. The large price increases in 1974 and 1975 for arsenicals were likely the result of large price increases for petrochemicals in these markets. The demand for arsenicals in the future is to a large extent dependent upon the price and availability of its petrochemical competitors.

5. The future for arsenical products lies to a great measure upon actions to be taken by a number of Government agencies. The Occupational Safety and Health Administration, the U.S. Environmental Protection Agency's Office of Pesticide Programs, and State agencies have the mechanisms for banning, severely restricting, or otherwise drastically influencing the demand for arsenicals or for their market competitors. The very threat of such Government actions has inhibited commercial activity on both the production and consumption sides.

6. The 1974 demand for white arsenic was estimated to be 24,000 metric tons, broken down as follows:

Insecticides	23 percent
Herbicides (Weed Control)	24 percent
Dessicants and Defoliants	15 percent
Soil Sterilizers	18 percent
Wood Preservatives	6 percent
Animal Feed Additives	2 percent
Glass Additives	10 percent
Miscellaneous Uses	2 percent

While the general category of pesticides includes 86 percent of the total white arsenic demand, the above breakdown indicates that no one specific use dominates the market.

7. Alternate (organic) insecticides are generally available, and in fact have taken over this market in which arsenicals were once dominant. The two remaining important applications for arsenical insecticides are for pest control on apples and for mosquito control.

8. Alternate organic herbicides for weed control are generally available. The two important markets for arsenical herbicides are for weed control on cotton lands and on turf.

9. The demand for arsenical dessicants in cotton harvesting in the Texas-Oklahoma region is growing, and there appear to be no totally-adequate substitutes.

10. Arsenical soil sterilizers are being used less frequently. Organic alternates exist.

11. Arsenical wood preservatives are increasing in demand, and there does not appear to be an adequate alternate in many applications.

12. Arsenical feed additives are important in the poultry industry; the antibiotic alternates are much more expensive.

13. White arsenic consumption in the glass industry has drastically decreased; its remaining uses are minor and specialized.

Dangers to Man and the Environment

1. The greatest threat to human health is the inhalation of airborne trioxide. The recent studies of airborne arsenic in the workroom, conducted relevant to the proposed revisions in OSHA standards, have resulted in the consensus that arsenic trioxide is a carcinogen, with lung and lymph cancer mortality rates for exposed workers 6 to 7 times the expected rates.

2. The major sources of arsenic pollution of the air outside of the workroom are the 40 to 50 primary non-ferrous metal smelters, particularly copper smelters. At distances of 10 to 15 miles from smelters, levels of arsenic in the air exceed the newly-proposed standards for the workroom. Dusts which have settled from the air near smelters contain hundreds of ppm of arsenic. Within the context that the areas influenced by smelter discharges represent only a small proportion of the Nation and of its population, the arsenic pollution of the air from smelters represents a public health hazard apart from the workroom considerations of OSHA.

3. Other than airborne emissions from primary non-ferrous smelters, important sources include secondary lead smelters, the many coal-burning electrical power generation stations, the production plants using white arsenic as a raw material, the emissions to the air from the use

and application of pesticides, and the incineration of cotton trash. All of these sources put together emit less arsenic than copper smelters, but these sources are much more dispersed in our population than the smelters.

4. Arsenic ingested via food, even in high concentrations in some sea foods, does not present any health threat yet identified. Although biomagnification of arsenic occurs in the food chain, the organic forms of arsenic in food are excreted within four days, with no identified hazard to humans. Arsenical feed additives for poultry and swine cause little if any accumulation of arsenic in the tissues of these animals; the Food and Drug Administration has set standards and monitors arsenic levels. The largest hazard from arsenic via foods appears to be inorganic arsenic on the surface of fruits and vegetables, either as insecticide residues on apples and some other fruits, or fallout from industrial and commercial point sources of air pollution.

5. Arsenic in water constitutes no current threat to the public health. Municipal water treatment plants are effective in reducing the arsenic content of raw water. The arsenic in fresh waters (resulting from natural or man-made erosion, from geothermal natural sources, from point sources of pollution, and from runoff from agricultural or suburban lands) becomes either locked into highly insoluble soil or sediment complexes where it is effectively removed as an environmental hazard, or it moves to the oceans. Very few public water supplies exceed the recommended maximum arsenic standard of 10 ppb.

6. The inorganic pentavalent forms of arsenic are 10 to 60 times less toxic than the inorganic trivalent forms. Moreover, organic compounds of arsenic are 10 to 100 times less toxic than inorganic compounds.

7. The use of arsenical pesticides and animal feed additives results in large quantities dissipated to land. These quantities are augmented by the arsenic in phosphate fertilizers, the fallout from sources of arsenic air pollution, and the large quantities of steelmaking slag that are used for various base and fill applications (although the arsenic in slag is likely fixed and insoluble as ferric arsenate).

8. Of the mobile arsenic dissipated to the land, chemical and bacterial actions serve to oxidize the arsenic over a period of time to the pentavalent state. Much of the pentavalent arsenic becomes bound as insoluble arsenates to iron oxide and aluminum oxide sites in clays. Some, as in the case of defoliated and dessicated cotton, is removed from the land via crop harvesting. Some is washed from the soil into surface waters, and some is leached and transported deeper into the soil. There is evidence that some organic arsenic is microbially changed to methylarsines, which volatilize from the land (and are subsequently oxidized to As_2O_3). As a cumulative result of these mechanisms, there is data to show the reduction with time of both total arsenic and available (soluble) arsenic in the soil after application of an arsenical.

9. Cacodylic acid is more resistant to oxidation than the sodium salts of methanearsonic acid (MSMA and DSMA). However, the microbially-aided oxidation of cacodylic acid is enhanced in "adapted" soils. All of these organic arsenicals are less toxic than inorganic arsenicals.

10. Competition of phosphorus with arsenic for available sites in soil renders arsenic relatively more soluble. Arsenic uptake by plants, and arsenic transport deeper into soil, is enhanced by phosphate fertilizers.

11. Since the largest uses of arsenicals are for non-food crops (cotton), for turf, and for other non-food applications, plant uptake is not a threat to human health. The use of arsenical insecticides on apples and other fruits has not resulted in arsenic levels which present a hazard. The tolerance of humans to organic arsenicals in foods, in combination with the above factors, negates the potential for a health hazard by arsenic in the food chain.

Control Alternatives Suitable for Reducing Dangers

Based upon the analyses in Sections III through VIII of this report, alternatives for controlling the emissions of arsenic and for reducing the hazards to health were formulated and are presented in Section IX. Also included in Section IX is an evaluation of these alternatives; several were screened out and rejected because they were not needed, not feasible, not effective, or too costly on an a priori basis. The control alternatives passing this screening process were then evaluated from a cost standpoint.

A summary of the control alternatives passing the screening process, each with a concise statement of feasibility, effectiveness, and cost, is included at the end of Section II.

SUMMARY OF CONTROL ALTERNATIVES

Control Alternatives	Feasibility	Effectiveness	Cost
Requiring effective (99+ %) removal of As_2O_3 from flue gases emitted to the atmosphere from copper smelters, other non-ferrous metal smelters, cotton trash incinerators, glass plants, and other industrial sources with As_2O_3 in high-temperature process gas streams.	Technology of removal using high-pressure-drop venturi scrubbers is demonstrated in gas-cleaning sections of by-product sulfuric acid plants.	Should reduce As_2O_3 emissions from 6,300 kkg/year by 99+ per cent, except for gases lost via leaks and spurious emissions. Other hazardous constituents would also be controlled.	Estimated capital cost of $8.3 million, plus $1.0 million/yr operating cost. Total cost is about $300 per kkg of As_2O_3 controlled.
Requiring environmentally-adequate land disposal of arsenic-containing slags, sludges, and collected flue dusts from industrial sources. Arsenic-bearing wastes from primary copper industry are 3/4 of all such wastes.	Technology of approved landfills, secured landfills, waste treatment, encapsulation, etc., has been demonstrated and is in practice.	Should protect 15,000 kkg/yr of arsenic in industrial wastes from migrating into environment via leaching, runoff, and wind dispersion. Other hazardous constituents in these wastes would also be controlled.	Estimated total cost for copper industry is $2.1 million/yr; of which $280,000/yr may be apportioned for control of arsenic. Cost is equivalent to $22 per kkg of As controlled.
Ban on the use of arsenical insecticides (calcium and lead arsenates, paris green).	Petrochemical alternatives available, but relative health hazard may be equal or greater, and relative insecticide effectiveness may be less.	Would prevent the dissipation of 5,500 kkg/yr of As_2O_3 equivalent; only the portion airborne during spraying application is hazardous.	Estimated costs would be $3.7 million first year, $3.4 million/yr next 4 years, $2.9 million/yr thereafter ($680, $630, and $530 per kkg of As_2O_3 diverted.
Ban on the use of arsenical desiccants and defoliants (arsenic acid).	Petrochemical alternatives do not appear to be adequate substitutes for Texas-Okla. cotton use, and relative hazard may be. equal or greater.	Would prevent the dissipation of 3,500 kkg/yr of As_2O_3 equivalent; the portion airborne during spraying and the portion emitted via incineration of cotton wastes are hazardous.	Estimated costs would be $2.4 million first year, $2.2 million/year next 4 years, $2.0 million/year thereafter ($680, $640, and $570 per kkg of As_2O_3 diverted).

Control Alternatives	Feasibility	Effectiveness	Cost
Ban on the use of arsenical herbicides for weed control (MSMA and DSMA).	Petrochemical alternatives are generally available, but relative hazard on cotton and turf may be equal or greater.	Would prevent the dissipation of 5,800 kkg/yr of As_2O_3 equivalent; the portion airborne during spryaing and the portion emitted via incineration of cotton wastes are hazardous.	Estimated costs would be $5.2 million first year, $4.3 million/year next 4 years, $2.9 million/year thereafter ($890, $740, and $500 per kkg of As_2O_3 diverted).
Ban on the use of arsenical soil sterilizers (sodium arsenite).	Petrochemical alternatives available, but use of arsenicals is highly selective. Relative hazards may be equal or greater.	Would prevent the dissipation of 4,200 kkg/yr of As_2O_3 equivalent; this quantity has not been shown to be hazardous.	Estimated costs would be $2.5 million/year first 5 years, $2.3 million/year thereafter ($600 and $560 per kkg of As_2O_3 diverted).
Ban on the use of arsenical wood preservatives (CCA & FCAP).	There do not appear to be adequate alternatives for many applications.	Would prevent the dissipation of 1,550 kkg/yr of As_2O_3 equivalent; this quantity has not been shown to be hazardous.	Estimated costs would be $2.4 million first year, $1.9 million/year next 4 years, $1.1 million/year thereafter ($1,570, $1,250, and $680 per kkg of As_2O_3 diverted).
Ban on the use of arsenical feed additives (Roxarsone & arsanilic acid).	Antibiotic alternatives exist but are much more expensive.	Would prevent the dissipation of 550 kkg/yr of As_2O_3 equivalent; this quantity has not been shown to be hazardous.	Estimated costs would be $1.2 million first year, $0.9 million/year next 4 years, $0.4 million/year thereafter ($2,250, $1,710, and $750 per kkg of As_2O_3 diverted).

Control Alternatives	Feasibility	Effectiveness	Cost
Ban on the use of As_2O_3 as an additive for glass (except for highly specialized infrared or scientific glasses).	Substitutes are available for oxidizing and fining.	Would prevent the dissipation of 2,400 kkg/yr of As_2O_3; only the portion emitted to the air (280 kkg/yr) during glass manufacture is hazardous.	Estimated costs would be $1.1 million/year for all years after ban ($460 per kkg of As_2O_3 diverted).
Total ban on the use of white arsenic and its derivatives (except for highly specialized and small-volume uses).	See feasibility of individual use bans.	See effectiveness of individual use bans. Would prevent the dissipation of 24,000 kkg/yr of As_2O_3.	Estimated costs would be $20 million first year, $16 million/yr next 4 years, $13 million/year thereafter ($830, $665, $550 per kkg of As_2O_3 diverted).
Requiring effective (99+ %) removal of As_2O_3 from flue gases emitted to the atmosphere from coal-burning electric power generating stations and other stationary sources.	Technology is similar as that for industrial sources of As_2O_3 emissions, but the concentration of As_2O_3 in coal-burning flue gases is much lower.	Should essentially eliminate airborne emissions of 650 kkg/year of arsenic, or 860 kkg/year of As_2O_3. Other hazardous constituents would also be controlled.	Extimated costs are $335 million/year. If total is apportioned among hazardous constituents, the cost for arsenic is estimated at $39,000 per kkg of As_2O_3 controlled.

OCCURRENCE AND CHEMISTRY OF ARSENIC

Natural Occurrence of Arsenic

The adjective most often used to describe the occurrence of arsenic is ubiquitous. The average crustal abundance is about 5 ppm (5 mg/kg, 0.0005 percent);(1,2,3) it is one of the less abundant elements (14th in abundance among trace elements), about on the same order of average crustal abundance as tin. Virgin soils usually contain only a few ppm of arsenic,(2) but soils having natural concentrations as high as 500 ppm have been reported.(4) Ferguson and Gavis(5) list concentrations of arsenic for the following rocks:

igneous rock	1.8 to 2.0 ppm
shale	6.6 to 10.0
sediments (deep sea)	10.0
sandstone and limestone	1.5

The greatest concentrations of arsenic occur with ores of copper, lead, cobalt, nickel, iron, and silver, either alone or with sulfur.(3) Lead, copper, and gold ores contain amounts of arsenic measured from trace amounts up to 5 percent.(1,2)

Three of the 15 copper smelters in the U.S. process ores having high arsenic content. The ASARCO smelter in Tacoma, Washington, processes ore containing 5.2 percent arsenic (52,000 ppm); the ASARCO plant at El Paso processes ore having an arsenic content of 0.96 percent, and the Anaconda smelter at Anaconda, Montana, processes ore containing 0.8 percent arsenic. The remaining copper smelters all process ore containing less than 0.2 percent arsenic.(19)

The arsenic content of zinc, lead, and copper ores is discussed in the section dealing with primary nonferrous metals. The arsenic content of zinc and lead concentrates from five foreign sources (data for American Ores is not available) averages 565 ppm for zinc concentrates (~50% Zn content) and 944 ppm for lead concentrates (66% Pb content). The arsenic content of copper concentrates have been measured at up to 16,000 ppm (Butte, Montana).(20) Unprocessed copper ore from Butte, Montana, has been measured to contain as much as 1000 ppm and 3700 ppm arsenic.(21,22) Thus arsenic is significantly concentrated above its average crustal abundance of 5 ppm in the ores of zinc, lead, and especially copper.

Gold ores in Sweden contain 7 to 11 percent,(1) and copper ore from the now-depleted Boliden deposit in Sweden contained an average of 10.8 percent arsenic - versus only 2 percent copper.(6) According to Swain, "not all sulfide ores contain arsenic, but wherever arsenic has been a source of trouble (e.g., pollution from smelting), sulfur has been present to aggravate it." The Boliden ore body contained about 30 percent sulfur.(6)

Over 150 arsenic-bearing minerals have been identified, of which the most common are the magmatic sulfides such as arsenopyrite (also called mispickel, $FeAs_2 \cdot FeS_2$), loellingite ($Fe_{2+x}As_{4-x}$), enargite ($3CuS \cdot As_2S_5$), realgar (AsS), and orpiment (As_2S_3). Magmatic sulfide ores contain an average of 2000 ppm of arsenic.(3) Veins of native arsenic have also been found in a number of localities.(1,3)

In sea water, according to Schneider, the "normal" concentration of arsenic is 0.003 mg/1, or 3 ppb.(4) Lansche places the concentration at 20 ppb and says that the arsenic exceeds the concentration of iron in sea water.(3) Sullivan cites 10 to 100 ppb as the arsenic concentration in seawater.(2) Ferguson and Gavis estimate the average concentration to be 2 ppb, "though measured values range from 0.15 to 6 ppb".(5)

Arsenic Content of Oceans(5)

	Concentration (ppb)
English Channel	2 - 4
Pacific Coastal Water	3 - 6
Northwest Pacific	0.15 - 2.5 (avg. 1.2)
Indian Ocean	1.3 - 2.2 (avg. 1.6)
Southwest Indian Ocean	1.4 - 5.0 (avg. 3.0)

Probably the single greatest source of arsenic in the earth's crust and in sediments and sedimentary rocks is the combined contributions of hot springs and volcanic activity. According to Reay,(22) hot springs in the Wairakei (New Zealand) geothermal field "are likely to be an important source of arsenic", because they are an important source of magmatic chlorine - which occurs in a fairly constant ratio with arsenic throughout the Pacific region. Reay calculated the natural output of arsenic in the Wairakei area to be on the order of 22 kkg/yr. Also, he noted that the bores for a geothermal power plant at Wairakei produced 190 kkg of arsenic in 1964, and "this can be expected to remain more or less constant".

Marine organisms tend to concentrate arsenic in their tissues. In sea water containing 0.05 to 5 ppb of arsenic, marine plants have been reported to contain between 1 and 12 ppm of arsenic (dry weight), while marine animals contain concentrations of 0.1 to 50 ppm. Arsenic in shrimp and lobsters, probably as trimethylarsine, has been measured as high as 200 ppm - a 100,000-fold increase over the average sea water concentration of 2 ppb.(5)

Arsenic occurrance is "very common in the freshwater of the western United States"; and in one part of the world, New Zealand, the naturally occurring arsenic in freshwater is reportedly sufficient to be lethal to animals (44 mg/animal kg).(4) Ferguson and Gavis report freshwater arsenic concentrations for various rivers and lakes throughout the world as follows:

Arsenic Content of Fresh Waters(5)

	Concentration (ppb)
Lakes in Greece	1.1 - 54.5
Lakes in Japan	0.16 - 1.9
Lakes in Wisconsin	2 - 56
Rivers and lakes in U.S.	10 - 1100
Rivers in Sweden	0.2 - 0.4
Rivers in Japan	0.25 - 7.7 (weighted avg. 1.7)
Elbe River, Germany	20 - 25
Columbia River, U.S.	avg. 1.6

The United States Public Health Service has established a recommended maximum concentration of 10 ppb and a maximum permissible concentration of 50 ppb for arsenic in public drinking water; both of these limits are well below the lowest reported concentration which resulted in chronic poisoning - 210 ppb.(5) Surveys of drinking water sources and supplies have been carried out over the years in the United States. In 1943, 37 drinking water supplies were tested for arsenic; the maximum concentration found was 8 ppb, and in 30 samples arsenic was undetected (<2 ppb). In 1969, a survey of 969 water supplies found that 0.5 percent of them exceeded the 10 ppb Public Health Service recommended limit and 0.2 percent of them exceeded the 50 ppb upper limit. In two studies of fresh surface waters in the United States in 1970 and 1971, arsenic was found in about 7 percent of 1500 samples from 150 rivers in one study, and in 21 percent of 727 samples from rivers and lakes in the other study. Although the limit of detection in these studies was at the P.H.S. recommended limit for drinking water, 10 ppb, most of the samples which had detectable arsenic were in the 10 to 20 ppb range. According to Ferguson and Gavis, there have been many observations of high concentrations of arsenic in lakes and impoundments in the United States, and they feel it is probable that arsenic concentrations in natural waters often approach or exceed values thought to be safe for drinking water.(5) A large portion of arsenic in surface waters of the United States is probably from other than natural sources; e.g., from arsenic in detergents, pesticidal runoff, and leachings from excavations and mining operations.

Arsenic also occurs, along with other trace materials, in coal and petroleum as well as in mine tailings and in products made from phosphate rock, such as fertilizers and detergents which are possible primary pathways of arsenic into the Nation's fresh water supplies.(7,8) Sullivan lists the arsenic content of coal burned in the U.S. at 0.08 to 16 ppm.(2) <u>The National Inventory of Sources and Emissions: Arsenic - 1968</u> gives a range of 1.18 to 9.95 ppm for domestic coal, with an average of 5.44 ppm,(9) on the order of the average crustal abundance.

According to Anderson(10), domestically-produced crude oil contains 0.007 to 0.61 ppm of arsenic, with an average concentration of 0.15 ppm; foreign crude contains from 0.01 to 0.34 ppm with an average of 0.13 ppm; and residual oils (i.e., crude oils for electric power generators and for the heating of buildings) contains 0.1 to 0.2 ppm arsenic with average of 0.14 ppm. The National Inventory of Sources and Emissions notes a group of 110 tests of domestic crude oil; in 97 of the tests arsenic was undetectable, but in 13 tests it ranged from 0.008 to 2.4 ppb, for an average concentration for all 110 samples of 0.042 ppm.(9) Oil from shale has been analyzed as containing 82 ppm of arsenic.(11)

The arsenic concentration in phosphate rock mined in the United States varies from values close to the average crustal abundance (about 5 ppm) up to 20 times this value. The arsenic content for commercial phosphate rocks has been cited by various researchers:

Reference	Florida Land Pebble	Florida Hard Rock (ppm arsenic)	Tennessee Brown Rock	Western Rock
(12)	3.5 - 22	1.5 - 11	5 - 56	4.5 - 105
(13)	7.5 - 37.5	3 - 9	15 - 30	7.5 - 112

Sauchelli(14) reports the arsenic content of "a representative analysis of 20-percent granulated superphosphate manufactured from Florida pebble rock phosphate" as 14 ppm. The Department of Agriculture(15) reports the arsenic content for 10 samples of industrial phosphoric acids as varying between 1.5 ppm and 1200 ppm, with the majority being in the area of 25 ppm, indicating that phosphate processing does not tend to remove the arsenic carried in the ore.

Since arsenate is chemically similar to phosphate, it is not unreasonable to think that arsenate might substitute for phosphate or at least to be fairly concentrated in phosphate minerals. However, in Florida phosphate pebbles, arsenic content is inversely proportional to phosphate content and directly proportional to the iron content, indicating that the affinity of arsenic for iron is the predominating concentrating factor for arsenic in phosphate.(5)

Domestic reserves of arsenic are estimated at 1.7 to 2.3 million kkg, approximately 40 percent of the known world reserves.(16,17,18) These values for domestic reserves are principally a function of copper reserves. Since arsenic is generally associated with magmatic deposits of complex base-metal ores, the reserves are probably significantly greater than the amount available as a by-product of copper production.(17,18)

Chemistry of Arsenic

Of the toxic elements, arsenic is probably the most well known. Pure elemental arsenic, however, is not very toxic, which is likely the result of its being virtually insoluble in water or in the body fluids. In fact, elemental arsenic is not readily attacked by water, alkaline solutions, or non-oxidizing acids; hydrochloric acid will attack it only in the presence of an oxidizer.(1)

Elemental arsenic is commonly referred to as a metal. Chemically, it is a nonmetal or metalloid being classified in Group 5a of the periodic table, along with nitrogen, phosphorus, antimony, and bismuth.

Properties of Arsenic(1)

Atomic number	33
Atomic weight	74.9216
Melting point	
at 1 atmos., sublimes at	613°C
at 28 atmos., melts at	817°C
Density at 20°C	5.72 g/cm^3
Latent heat of fusion	88.5 cal/g
Latent heat of sublimation	102 cal/g
Specific heat at 20°C	0.082 cal/(g) (°C)
Lattice constants at 26°C	a = 2.760A b = 10.548A
Hardness (Mohs' scale)	3.5

There is only one stable arsenic isotope; therefore, the natural abundance of ^{75}As is 100 percent. The electron configuration is such that the five electrons in the outer shell give rise to the three principal oxidation states which are -3, +3, and +5.(1)

Elementary arsenic occurs in three allotropic modifications. They are the yellow, the black, and the metallic or gray forms, the latter being the most stable at room temperature. The electrical conductivity of the metallic form at 0°C is 2.56×10^4 mhos/cm, about half that of lead. The other allotropic modifications are listed as nonconductors.(23)

The yellow form of elemental arsenic can be produced by passing arsenic vapor into cold carbon disulfide and cooling the solution to -70°C. This yellow form is an extremely volatile solid, subliming even from the heat of the hand. Its density is 3.9 g/cm^3, and its molecular weight corresponds to that of tetrahedral As_4 molecules. It is metastable and transforms into the metallic form even at low temperature; in sunlight, at room temperature, it changes virtually instantaneously.(24,25)

The black modification of elemental arsenic is not as well characterized as the other forms. It is obtained by the thermal decomposition of arsine, AsH_3. The density of black arsenic is 4.7 g/cm^3. Its molecular configuration is not definitely known, but it is probably tetrahedral.(24)

Metallic arsenic forms hexagonal-rhombic crystals and cubic crystals. It is stable in dry air, but exposure to humid air causes the surface to tarnish, first to a bronze color then to black.(1) The density of the metallic form is the highest for the three allotropic modifications: 5.72 g/cm^3. Metallic arsenic is the common commercially-available form, being the product of the reduction of arsenic trioxide with coke according to

$$As_4O_6 + C \xrightarrow[\Delta]{} As_4 + 6CO$$

It can also be sublimed from arsenopyrite according to

$$4FeAsS \xrightarrow[\Delta]{} 4FeS + As_4$$

When heated in air elemental arsenic sublimes and oxidizes to arsenic trioxide. A garlic-like odor is produced during the oxidation process.(1) At about 200°C it becomes phosphorescent. At about 400°C it burns with a bluish flame and produces white smoke which is, of course, arsenic trioxide.(1,24) In the vapor state up to 800°C, elemental arsenic consists of As_4 molecules having a tetrahedral structure. Above 800°C, it begins to decompose to As_2, and at still higher temperatures, it becomes monatomic.(24)

Though the common oxidation states are +3, +5, and -3, other oxidation states are known. Examples are the polyarsenides Na_3As_3, Na_3As_5, and Na_3As_7 and a series of naturally occurring copper minerals ranging in composition from Cu_3As to Cu_9As.(26) Compounds or solutions containing the simple ions As^{3-} and As^{5+} do not exist because of the high energy requirements for acquiring three electrons or for ionization of five electrons.(26)

In most compounds, arsenic exhibits a coordination number of 4, based on tetrahedrally hybridized orbitals. Even the molecules AsH_3 and $AsCl_3$, where the arsenic coordination number is 3, are assumed to be tetrahedral with a lone pair of electrons in one of the hybrid orbitals.(25,26)

Similarity to Phosphorus

As a member of Group 5a of the periodic table, the physiochemical properties of arsenic are closely related to those of phosphorus. Arsenates strongly resemble the corresponding phosphates in solubility and crystal form, many phosphate-arsenate pairs being isomorphous. Arsenic also forms trihalides analogous to those of phosphorus, and the arsenate ion reacts with ammonium molybdate in nitric acid solution as does the phosphate ion. Generally, arsenates are much more labile than corresponding phosphates, a fact important in the chemical and biologic reactions within which both elements may participate.(27)

Determination of Arsenic

The three most frequently used methods for the determination of arsenic are:

1. Gravemetric determination as either As(+3) or As(+5) sulfide which has been precipitated from an acidic solution by H_2S.
2. Precipitation of silver arsenate with subsequent determination of silver by Volhard's method.
3. Iodometric titration of As(+3) in the presence of sodium bicarbonate.

To detect small quantities of arsenic, the Marsh test is used. The arsenic-containing material is mixed with granulated zinc, and dilute sulfuric acid is added. The zinc reacts with the acid to release hydrogen which reduces the arsenic to gaseous arsine, AsH_3. The arsine is then decomposed in a hot glass tube giving a mirror of elemental arsenic. Arsine can also be detected in a gas mixture by its reducing action on silver nitrate or mercury (+2) chloride.

This is called the Gutzeit test, and the amount of silver nitrate or mercury chloride reduced corresponds to the amount of arsenic present in the substance being measured.(24) Accuracies of these methods are 5 to 10 percent, and limits of detection are on the order of 0.080 μg.(1)

Highly accurate procedures (having limits of detection on the order of 0.001 μg) based on the determination of arsenic as arsine in an electric discharge have been developed. These procedures permit the determination in aqueous solution of arsenite ion and arsenate ion, as well as of the organic species methylarsonic acid and dimethylarsinic acid (both of which are discussed more fully below).(28)

Other highly accurate and precise procedures for measuring trace amounts, though sometimes they are time consuming, include neutron activation analysis (having a limit of detection near 0.001 μg), emission spectroscopy, and polarographic techniques.(5,28)

Inorganic Compounds

The most important commercial arsenic compound is arsenic trioxide, also known as arsenous oxide, "white arsenic", and (as a misnomer) arsenic. It occurs as an octahedral crystal of As_4O_6 molecules. The dissociation to As_4O_6 can be detected at temperatures of about 800°C. At a temperature of 1800°C, the molecular weight is that of As_2O_3.(26) Generally, however, the formula, As_2O_3, is the one commonly applied, regardless of temperature.

Arsenic trioxide is a white solid (the commercial form is a white powder) having a melting point of 275°C, though it begins to sublime at 135°C. It is amphoteric and therefore soluble in both acids and bases, and is soluble in water to the extent of 2 g/100ml water at 25°C and 11.5 g/100ml at 100°C. Molecular weight is 197.82 (76 percent As), and specific gravity is variable, 3.74 to 4.15.(29)

When arsenic trioxide is dissolved in water it forms arsenous acid, the exact nature of which is not known; representative chemical formulas which have been used include H_3ASO_3, $HAsO_3$, and As_2O_3 (aq). It is a weak acid having a dissociation constant of 8×10^{-10} at 25°C. H_3AsO_3 is also thought to exist as the hydroxide $As(OH)_3$ which may explain the ability of arsenic trioxide to neutralize both acids and bases:

$$As(OH)_3\ (s) + H^+ \rightarrow As(OH)_2^+ + H_2O$$

$$As(OH)_3\ (s) + OH^- \rightarrow H_2AsO_3^- + H_2O$$

That only one dissociation constant is given for arsenous acid supports the hypothesis that three hydroxyl groups are attached to the arsenic atom in the free acid.(26) The salts of arsenous acid are known as arsenites (As(+3) salts).(30)

The other commercially important oxide of arsenic is arsenic pentoxide, (also referred to as arsenic oxide). It is a white amorphous powder having a molecular weight of 229.82 and a specific gravity of 4.086.(29) Its chemical structure is not known, though it is probably dimeric, As_4O_{10}. The empirical formula generally used is As_2O_5. The compound begins to decompose into a vapor as As_2O_3 and O_2 at a temperature of about 300°C. It is very soluble in water, though it dissolves slowly. Solubility is on the order of 2300 g/liter of water at 20°C.(30)

In water, arsenic pentoxide forms arsenic acid (orthoarsenic acid), H_3AsO_4, a triprotic acid having three dissociation constants (as does phosphoric acid). $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5.6 \times 10^{-8}$, and $K_3 = 3 \times 10^{-13}$. The salts of arsenic acid are known as arsenates (As(+5) salts); they are good oxidizing agents.(30)

Arsenic pentoxide is commercially prepared by the dehydration of crystalline arsenic acid which is itself prepared by crystallization of a solution of arsenic trioxide and concentrated nitric acid. The dehydration of the crystalline arsenic acid takes place at about 200°C according to

$$2H_3AsO_4 \xrightarrow{\Delta} 3H_2O + As_2O_5$$

Arsenic pentoxide cannot be prepared by the reaction of its constituent elements or by the reaction of arsenic trioxide with oxygen.(26,30)

The arsenates can be reduced by concentrated hydrochloric acid or sulfur dioxide. Treatment of a solution of orthoarsenate with silver nitrate in neutral solution results in formation of a dark-brown precipitate of silver orthoarsenate, a method of distinguishing between arsenates and phosphates.(30)

The most common arsenic hydride is arsine, AsH_3, also known as hydrogen arsenide and arsenic trihydride. It is a colorless gas, but it has a characteristic garlic odor. Vapor density is 2.7 times that of air. (An atmospheric concentration of 1 mg of arsine per cubic meter of air corresponds to 0.313 ppm at 25°C and standard pressure). The melting point of arsine is -116.3°C and the boiling point is -62.4°C. Its solubility in water is 200 ml/liter at room temperature. Of all arsenic compounds, simple AsH_3 and its methyl derivitives are the most toxic.(26,30)

Arsine is the product of the reaction between atomic hydrogen and arsenic; however, the reaction cannot be carried out by the direct union of arsenic and hydrogen because arsine is not stable and will decompose well below 300°C. Arsine is formed whenever any inorganic arsenic-containing material is reacted with zinc and strong acids. Pure arsine can be condensed at low temperatures from a dried gas stream produced by a reaction of arsenic pentoxide with hydrochloric acid and zinc.(26,30)

Exposure to arsine gas may result from the action of acids on metals containing arsenic, from the use of impure sulfuric acid made from pyrites containing arsenic, or from the use of hydrochloric acid made from impure sulfuric acid that contains arsenic. Arsine poisoning has resulted from slushing out steel tanks that had previously contained a commercial grade of sulfuric acid, the diluted acid acting upon the metal tank to generate hydrogen, which combines with arsenic impurities in the acid. Arsine may arise from the pickling of any metal containing arsenic; it has been formed from the action of water on metallic arsenides or hot dross containing arsenic and aluminum. Arsine may occur as an impurity in acetylene and may present a hazard either in its manufacture or use. It may occur in soldering, etching, lead plating, electrolysis of arsenious solutions, by the action of moisture on ferrosilicon, or from the use of impure or inhibited acids for scale removal. According to Patty, the faint garlic-like odor of arsine cannot be considered a suitable warning property. The 1961 ACGIH threshhold for arsine is 0.05 ppm.(29)

Arsine is a good reducing agent, capable of reducing many substances. It is not oxidized by air at room temperatures but may be ignited with the formation of either arsenic trioxide or arsenic pentoxide, depending upon the supply of air. Arsine reduces dilute silver nitrate solution with the formation of metallic silver; with concentrated silver nitrate solution, a complex, $Ag_3As \cdot 3AgNO_3$, is formed which yields metallic silver when diluted with water. Mercury (+2) chloride is reduced stepwise forming initially the yellow compound, $AsH(HgCl)_2$, then the brown $As(HgCl)_3$ and, finally, black As_2Hg_3. Chlorine reacts with arsine to produce hydrogen chloride and arsenic. However, at low temperatures, the action of chlorine upon arsine produces chloroarsines, AsH_2Cl and $AsHCl_2$, both of which are relatively unstable yellow solids.(26)

Two other arsenic hydrides have been reported, but their exact chemical natures have not yet been determined. Reduction of trivalent arsenic compounds by tin (+2) chloride in hydrochloric acid yields a brown amorphous powder corresponding to the composition As_2H_2 (or AsH). This material is soluble in nitric acid but not in water, alkalies, or other acids. It reduces silver nitrate and the salts of other heavy metals. Treatment with boiling water causes evolution of hydrogen and the formation of arsenic oxide. It is thermally unstable and decomposes when heated in a vacuum to form metallic arsenic and some arsine. The other solid arsenic hydride is reported to have the formula As_4H_2 and is formed by oxidation of arsine with tin (IV) chloride.(26)

The mono-, di-, and trimethylated forms of arsine are discussed below in the Organic Compounds portion of this section.

The three arsenic sulfides are arsenic (+3) sulfide (arsenous sulfide, arsenic sesquisulfide, arsenic red), arsenic sulfide (arsenic monosulfide, arsenic disulfide), and arsenic (+5) sulfide (arsenic pentasulfide).(30)

Arsenic (+3) sulfide (As_4S_6, As_2S_3) has a melting point of 320°C and a boiling point of 707°C. Like many arsenic compounds, sublimation takes place before melting. It is insoluble in acid and almost insoluble in water (0.52 mg/

liter at 18°C), but it dissolves readily in many basic solutions. It will burn in air, forming arsenic trioxide and sulfur dioxide.(30)

Arsenic sulfide (As_4S_4,As_2S_2,AsS) occurs naturally as realgar. It has a melting point of 307°C and a boiling point of 565°C. Arsenic sulfide is listed as insoluble in water and in hot concentrated hydrochloric acid, though it is soluble in warm alkali hydroxide and sulfide solutions. The compound can be oxidized by nitric acid and will react vigorously with chlorine.(26)

Arsenic (+5) sulfide (As_2S_5) is a stable compound at room temperature, but at temperatures above 95°C it dissociates into arsenic (+3) sulfide and sulfur. It is soluble in water to the extent of 3 mg/liter, and in boiling water it is hydrolyzed yielding sulfur and arsenous acid. It is soluble in basic solutions and in nitric acid. It can be precipitated at low temperatures from strong acidic solutions which contain arsenates by bubbling hydrogen sulfide through the solution at a rapid rate.(26)

Arsenic forms a complete series of trihalides, but arsenic (+5) fluoride is the only simple pentahalide known. Whitacre and Pearse cite the reference of Hodgman, et al, to the possible existence of arsenic pentachloride and pentaiodide, though such existence is believed unlikely.(30)

Unlike phosphorus and antimony, arsenic forms no well-characterized oxyhalides, but arsenyl chloride, AsOCl, and arsenyl bromide, AsOBr, are considered likely to be present in the brownish material formed by treatment of arsenic trioxide with the corresponding trivalent arsenic halide. All of the arsenic halides are covalent compounds that hydrolyze in the presence of water. The trihalides form pyramidal molecules similar to trivalent phosphorus analogs and may be prepared by direct combination of the elements.(26)

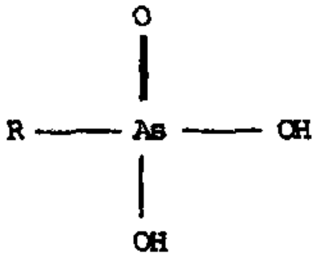
Arsenic fluoride (AsF_3) and arsenic chloride ($AsCl_3$) are both colorless liquids at 25°C, whereas arsenic bromide ($AsBr_3$) is a yellow solid and arsenic iodide (AsI_3) is a red solid. Arsenic (+5) fluoride (AsF_5) is a colorless gas at 25°C, though it can be condensed to a yellow liquid.(5) Arsenic halides are soluble in non-polar solvents such as benzene and carbon disulfide.(25)

Arsenic forms compounds with most metals, a number of which are naturally occurring, such as safflorite ($CoAs_2$), nicoolite ($NiAs$), rammelsbergite ($NiAs_2$), loellingite ($FeAs_2$), and sperrylite ($PtAs_2$). In addition, minerals containing arsenic, sulfur, and one or more metals such as arsenopyrite ($FeAsS$), cobaltite ($CoAsS$), glaucodot ((Co, Fe)AsS), and gersdorffite ($NiAsS$) are well known. Many of the metallic arsenides may be prepared by the direct combination of the elements. These compounds frequently resemble alloys and may consist of giant molecular lattices. The apparent oxidation number of arsenic in many of these compounds is frequently unusual.(26)

Arsenic generally behaves as an anion in the form of arsenites and arsenates. There are no arsenic carbonates, bicarbonates, or phosphates. The only major inorganic compounds in which arsenic acts as a cation are the halides and sulfides. There is an arsenic monophosphide (AsP) which dissociates in water, and arsenic (+3) sulfate ($(As_2SO_4)_3$) which is formed by the reaction of arsenic trioxide and SO_3 at a temperature of 100°C. Arsenic (+2) sulfate is soluble in water.(30)

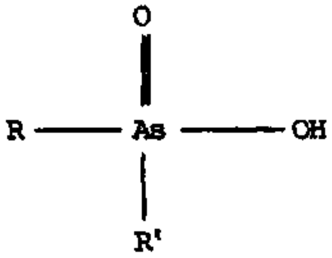
Organic Compounds

The largest class of arsenical compounds are the organic compounds. They are seldom found in nature — most have been synthesized, largely in an effort to find compounds having therapeutic value. Of the large number of organic arsenicals the two most common are the arsonic acids and the arsinic acids. Their structural formulas being:



$$R - \underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}} - OH$$

Arsonic Acid



$$R - \underset{\underset{R'}{|}}{\overset{\overset{O}{\|}}{As}} - OH$$

Arsinic Acid

The R and the R' refer to a variety of organic groups, and although there are many derivatives of these two acids, only cacodylic acid (dimethylarsinic acid) and methanearsonic acid (also referred to as methylarsonic acid) and its salts are widely used, mostly as herbicides.(31)

Methanearsonic acid and cacodylic acid are relatively strong acids, capable of decomposing carbonates. Methanearsonic acid is a dibasic acid, forming both a monosodium acid salt and a disodium salt with sodium hydroxide. Cacodylic acid is normally monobasic, but in strong sodium hydroxide solution it forms the disodium salt, $(CH_3)_2AsO_3HNa_2$, of a tribasic acid. Cacodylic acid is somewhat amphoteric, forming a hydrochloride, $(CH_3)_2AsO_2H \cdot HCl$, by direct reaction with hydrogen chloride gas.(31)

Both of these organic acids contain arsenic in the fully oxidized pentavalent state, so only the methyl groups can be further oxidized. This requires a strong oxidizing agent such as a nitric-sulfuric acid mixture. The end product is orthoarsenic acid.(31)

Methanearsonic acid and its salts can be reduced with mild reducing agents such as nascent hydrogen and sulfur dioxide to form arsenosomethane, CH_3AsO, a trivalent organic arsenical. Cacodylic acid and its salts can also be reduced to form cacodyl oxide $(CH_3)_2AsOAs(CH_3)_2$, also a trivalent organic arsenical, although a much stronger reducing agent, such as phosphorous acid, is required.(31)

Reduction of arsonic acids with mild reducing agents gives either the arsonous acids, $RAs(OH)_2$, or their anhydrides, $(RAsO)_x$, termed arsenoso compounds. With aliphatic arsonic acids or with aromatic arsonic acids in which the ring is unsubstituted or substituted with electron-repelling groups, the arsenoso compounds are the reduction products. With aromatic arsonic acids containing electron-attracting groups, the arsonous acids are usually obtained. The usual reducing agent is sulfur dioxide and hydriodic acid. The actual reduction is accomplished by the hydriodic acid and the resulting iodine is reduced again to hydriodic acid by the sulfur dioxide. Sulfur dioxide alone is used in some cases. The reaction is usually carried out in hydrochloric acid solution in which case the actual reduction product is the dichloroarsine, $RAsCl_2$. These, however, are readily hydrolyzed, either by alkali or by water alone, to the arsonous acid or the arsonoso compound. The arsonous acids are weak acids. Both arsonous acids and arsenoso compounds dissolve in strongly alkaline solutions, but their salts have not been isolated.(26)

The reduction of arsinic acids under the same conditions used for the reduction of arsonic acids gives either the arsinous acids, R_2AsOH, or their anhydrides, $(R_2As)_2O$. These same compounds can also be prepared by the reaction of arsenic trioxide with Grignard reagents. The anhydride of dimethylarsinous acid, $(CH_3)_2AsOAs(CH_3)_2$, is cacodyl oxide, which is of historical interest since it was the first organic arsenical ever synthesized.(26)

Dihaloarsines, $RAsX_2$, and monohaloarsines, R_2AsX, may be prepared by a wide variety of methods including reduction of arsonic acids in hydrohalic acid solution with sulfur dioxide and hydroiodic acid. They may also be obtained from arsenic trichloride and organometallic compounds such as the organic mercurials or organo-lead compounds.(26)

When acetylene is passed into arsenic trichloride solution in the presence of a catalyst such as aluminum chloride or mercury dichloride, a mixture of three products, $ClCH{=}CHAsCl_2$, $(ClCH{=}CH)_2AsCl$, and $(ClCH{=}CH)_3As$, is obtained. These are the "lewisites", after the American Chemist W.L. Lewis; the first of the three is colorless or brown in the liquid state, and because of its powerful vesicant qualities has been proposed as a war gas.(26)

Diazomethane can be reacted with arsenic trichloride to form chloromethyl-dichloroarsine and bis(chloromethyl)chloroarsine. In addition to these haloarsines, other compounds of the types $RAsX_2$ and R_2AsX, where X is a group such as cyano, thio-cyano, or cyanato, can be formed. They can be formed by metathesis between the halorarsine and a silver or sodium salt.(26)

The reduction of arsonic acids with stronger reducing agents gives arseno compounds having the empirical formula RAs. Appropriate reducing agents of these compounds include sodium hydrosulfite and hypophosphorous acid. Electrolytic reduction has also been used for the preparation of arseno compounds. The arseno compounds were at one time widely used in medicine, but not any longer.(26)

The reduction of arsinic acids and other arsenicals containing the R_2As grouping gives secondary arsines, R_2AsH. Dimethylarsine can also be prepared from $Ca(AsH_2)_2$ and methyl chloride. Diphenylarsine can also be prepared by the action of water on the Grignard reagent, $(C_6H_5)_2AsMgBr$. Primary and secondary arsines are readily oxidized in air and must be preserved in an inert atmosphere.(26) They are very toxic.

According to Doak,(26) the tertiary arsines, of the form R_3As, are "more important" than the primary or secondary arsines. Several methods of preparation are given. Trimethylarsine is a byproduct of the action of certain molds growing on a suitable substrate of arsenical compounds. Methylarsines, especially trimethylarsine, have been included in various natural cycles in soil and fresh water. These cycles are discussed below.

Arsenic also forms a series of pentavalent chloro-compounds of the form $RAsX_4$, R_2AsX_3, and P_3AsX_2. Compounds of the type $RAsX_4$, where R may be either aliphatic or aromatic, are not very stable and have not been thoroughly investigated. Compounds of the type R_2AsCl_3 are more stable than the tetrachlorides. The reaction of tertiary arsines, both aliphatic and aromatic, with halogens to give compounds of the type R_3AsX_2 has been studied extensively. When one of the R groups is methyl, these compounds readily lose methyl chloride on heating to give chloroarsines.(26)

In addition to the dihalides, mixed compounds of the type R_3AsXY are known, in which X and Y are two different groups. Thus, the reaction of dimethylphenylarsine with hydrochloric or nitric acid in the presence of hydrogen peroxide gives the hydroxychloride, $(CH_3)_2C_6H_5As(OH)Cl$, or the hydroxynitrate, $(CH_3)_2C_6H_5As(OH)NO_3$, respectively.(26)

Oxidation of the tertiary arsines gives either the arsine oxides, R_3AsO, or the arsine dihydroxides. Arsine sulfides of the type R_3AsS have also been prepared.(26)

The organic chemistry of arsenic is complex and involved, and the reader interested in further information is referred to excellent summary by Doak, et al, in the <u>Encyclopedia of Chemical Technology</u>; an extensive bibliography is included.

Various trivalent organic preparations of arsenic have been used, mostly in the first half of this century, for the treatment of syphilis, trypanosomiasis (sleeping sickness), spirochetal infections, amebic dysentery, psoriasis, and even leukemia. Nowadays, however, arsenical compounds find little use in medicine either because of the toxic hazards of the arsenicals or because more specific medications having lesser side effects are available.

Arsenic Adsorption and Coprecipitation

Arsenic can be fairly easily separated from other elements, and can be removed from solutions by adsorption and coprecipitation. Arsenic can be precipitated in the elemental state by reducing agents such as hypophosphite or stannous chloride. Hypophosphite has been used to precipitate arsenic from solutions of 1:1 hydrochloric acid, with a recovery of about 95 percent when copper is present to catalyze the reduction.(30)

Pentavalent arsenic, which includes arsenates, can be coprecipitated with ferric hydroxide or magnesium ammonium phosphate. In the former case, it is believed that the arsenates adsorb onto the surface of the hydrous iron oxides.(30) Ferguson and Gavis report that iron ores are enriched with arsenic because of the high adsorptive capacity of the hydrous iron oxides. Iron oxide has a positive surface charge and therefore adsorbs anions.(5) Since arsenic exists primarily as anionic arsenate and arsenite species in solution, it can be adsorbed on the positively charged iron oxide surfaces.(30) Arsenates can also be adsorbed by aluminum hydroxides and clays.(5)

Trivalent arsenic has a strong affinity for sulfur and will coprecipitate with metal sulfides. Arsenic trisulfide, As_2S_3, is insoluble in hydrochloric acid, and, hence, precipitation by hydrogen sulfide from a 25-percent solution of HCl is used as a method of qualitative analysis for the presence of arsenic in solution. The technique of adsorption of arsenites onto hydroxides and clays is, according to Whitacre and Pearse, a promising candidate for arsenic water pollution abatement.(30) Adsorption and coprecipitation processes are discussed in the sections below dealing with water and soil chemistry.

White Arsenic Refining

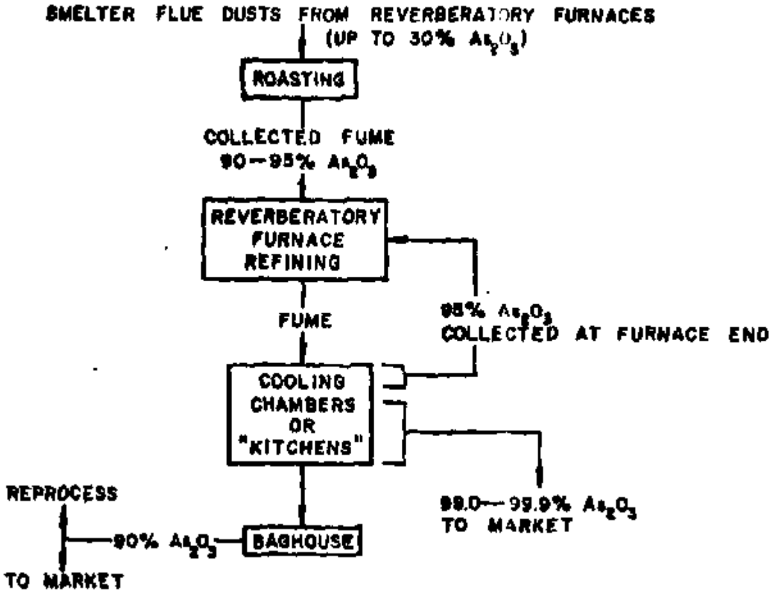
The precursor material for virtually all arsenical compounds is arsenic trioxide, or white arsenic, as it is more commonly known in the trade. In the United States the only producer of white arsenic is the American Smelting and Refining Company, and their arsenic refining operations are carried out at Tacoma, Washington, where ASARCO has the facilities for the smelting of copper ores and other base-metal ores containing large portions of sulfur and arsenic. The arsenic refining portion of the plant is unique in comparison to other mined-mineral production facilities in that the arsenic trioxide is recovered as a flue-dust byproduct from other smelting operations; it is this relatively volatile dust which must be purified. ASARCO processes its own flue dusts, which contain as much as 30-percent arsenic plus other oxides of perhaps copper, lead, zinc, and antimony. ASARCO also processes the flue dusts of other base-metal producers both in this country and abroad. Carapella's description of white arsenic refining, in the Encyclopedia of Chemical Technology, is the one most commonly referred to in studies of arsenic:(1)

> Because arsenic trioxide is readily volatilized during the smelting of copper and lead concentrates, it is concentrated with the flue dust. This crude flue dust is further upgraded by mixing with a small amount of pyrite or galena concentrate and roasting. The pyrite or galena is added to prevent arsenites from forming during roasting and to obtain a clinkered residue which can be returned for additional processing. The gases and vapors are passed through a cooling flue which consists of a series of brick chambers or rooms called kitchens. The temperature of the gas and vapor is controlled so that they enter the first kitchen at 200°C and by the time the gas and vapor reach the last kitchen they are cooled to 100°C or less. The arsenic trioxide vapor which condenses in these chambers is of varying purity. The condensed product is obtained by resubliming the crude trioxide. The resubliming operation is normally carried out in a reverberatory furnace. The vapors pass first through a settling chamber and

then through approximately 39 kitchens that cover a length of about 225 feet. The temperature of the settling chamber is kept at approximately 295°C, which is above the condensation temperature of the trioxide. A black, amorphous mass containing about 95 percent As_2O_3 condenses in the kitchens nearest the furnace and is reprocessed. The bulk of the trioxide is condensed in the kitchens with temperature ranges of 180-120°C. The purity of the arsenic obtained from these kitchens is from 99 to 99.9 percent. The dust which exits from the kitchens as a temperature of 90-100°C is caught in the baghouse. It assays about 90 percent As_2O_3 and may be sold as a crude arsenic or reprocessed.

The refined arsenic is analyzed for purity. It is also treated for "solubility", a term referring to its rate of reactivity with nitric acid; this test is important if the arsenic is used in the manufacture of insecticides and herbicides. The product is graded for marketing as white soluble (99 percent min. As_2O_3), white insoluble, or crude (95 percent min. As_2O_3).

The diagram below is a schematic flow diagram of the operations in the refining of arsenic trioxide.



Chemistry of Arsenic in Fresh Water

The chemistry of arsenic in aquatic systems is complex, involving oxidation-reduction, microbial intervention, and adsorption and coprecipitation reactions, among others, and not all of it is well understood. Ferguson and Gavis, in their paper, A Review of the Arsenic Cycle in Natural Waters(5), have devised a diagram showing the regions of stability of various inorganic arsenical species (e.g., arsenic acid in various states of dissociation) as a function of pH and oxidation condition of water. With regard to the organic arsenicals, they state that except under very reducing conditions in water, the organic component of the arsenicals will undergo oxidation.

The equilibrium conditions of inorganic arsenic in solution are well understood, but except for a few oxidation-reduction reactions as are used in analytical chemistry, very little is known about the rates of arsenic reactions in solution, and specific rate constants are unknown. For example, the rate of oxidation of arsenite to arsenate with O_2 is reportedly very slow at neutral pH values, but in strongly acid or alkaline solutions the reactions proceed measureably in several days unless copper salts and carbon are available in the system to catalyze the reaction. No quantitative information is available about the rate of such reactions in aerobic waters, according to Ferguson and Gavis.

Inorganic arsenic in water is commonly analyzed by means of colorimetric methods based on colored complexes formed with diethyldithiocarbamide or molybdate. Other analysis methods include neutron activation, atomic absorption and emission spectroscopy, and polarographic methods. Colorimetric and polarographic methods can also be used to determine oxidation states in inorganic arsenic.

A lack of suitable analytical chemical procedures has hampered studies of arsenic in water, especially the determination of the inorganic arsenic ions and the methylarsinic acids at very low concentrations. Most methods used for the determination of arsenic in low concentrations measure the total elemental concentrations, and many depend on the reduction of inorganic arsenic ions to arsine and subsequent colorimetric analysis. The lower limit of detection of the silver diethyldithiocarbamate method is not lower than 0.2 µg, and though neutron activation methods have a limit of detection of near 0.001 μg they are relatively time consuming. The methods employed by Braman and Foreback have enabled them to distinguish arsenite, arsenate, methylarsonic acid, and dimethylarsinic acid to lower limits of detection of near 0.001 μg. Their procedures depend upon pH selective reduction reactions of the various arsenic forms with sodium borohydride and a separation of the volatile arsines produced by selective volatilization from a cold trap.(28)

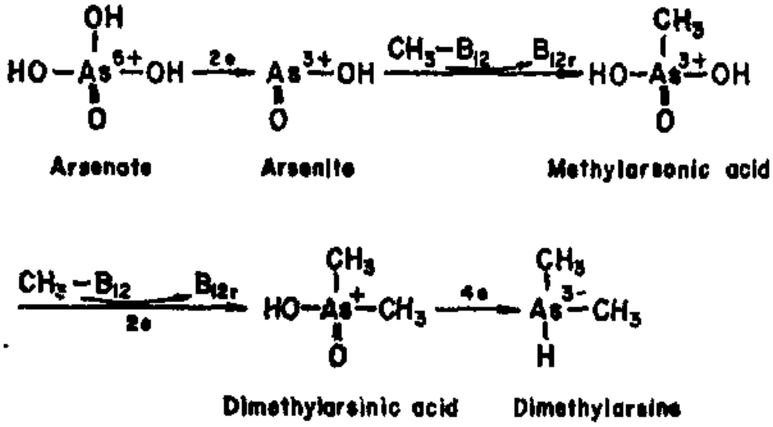
Arsenic forms stable bonds with sulfur and carbon in organic compounds. As is discussed in the Toxicology portion of this study, it is the affinity of trivalent arsenic (arsenite) for sulfhydryl groups, most notably in the amino acid cysteine in proteins, and the resultant enzyme inactivation, which accounts for the primary mode of arsenic toxicity. Pentavalent arsenic (arsenate) does not react with sulfhydryl groups, but reduction of arsenate to arsenite can take place within organisms both large and small, and, in the case of certain waterborne fungi, according to Challenger (as reported by Braman and Foreback), such reduction processes in natural waters could cause an increase in the ratio of more harmful arsenite to less harmful arsenate.(28)

The methylarsines are an important group of arsenical compounds within natural systems. Mono-, di-, and trimethylarsines, and even simple arsine have reportedly been synthesized by such organisms as yeast, fungi, and bacteria.(5,8,28,37) The proposed metabolic processes producing these arsines are based on both inorganic and organic arsenical precursors, and have been stated to occur in both aerobic and anaerobic settings. Microbiological processes have also been identified as the sources of other methylated arsenicals, most notably the methylarsonic and dimethylarsinic acids, which themselves are included in biological cycles which include the synthesis of methylarsines.(8,28,33)

Trimethylarsine has been identified as an important reservoir of arsenic in certain organisms.(5) And although it is considered insoluble in water, Ferguson and Gavis cite it as being sufficiently soluble to be of environmental interest, especially since it has caused human poisoning in its vapor phase in air. It is more soluble in hydrocarbons than water, which may account for its accumulation in the fatty tissues of certain aquatic organisms. However, neither its stability with respect to oxidation by oxygen in air or in water, nor its adsorptive behavior appear to have been studied.(5)

Braman and Foreback(28) report that a large portion of arsenic that is found in human urine (up to 90 percent) is methylated. They suggest this may be the result of a biological defense mechanism against the much higher toxicities of inorganic arsenates and especially arsenites which are 25 times more toxic than dimethylarsinic acid. The methylated types of arsenic in urine are dimethylarsinic acid (cacodylic acid) and methylarsonic acid (which is the same as methanearsonic acid, the sodium salts of which are the herbicides DSMA and MSMA).

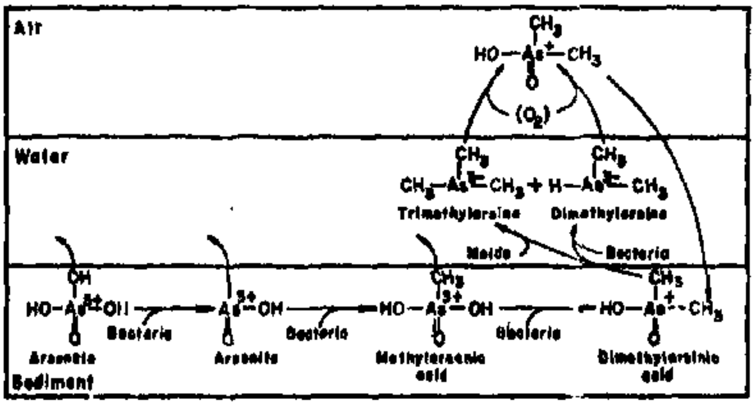
Methylation of arsenic by bacteria has been studied by Wood and by McBride and Wolfe.(8,28,33) McBride and Wolfe have shown that anaerobic bacteria can produce mono- and dimethylarsine from a variety of arsenic compounds, and they have suggested a cycle in which methylcobalamin serves as the methyl donor in the reaction system. (Methyl cobalamin is also cited by Braman and Foreback as the methyl donor for the methylated arsenic found in human urine, the reaction presumably taking place within the body.) Arsenate is first reduced to arsenite which is then methylated to methylarsonic acid which is further methylated to form dimethylarsinic acid which in turn finally becomes dimethylarsine. The diagram below illustrates the process of methylation.(8)



CH_3-B_{12} = Methyl cob(III)alamin

B_{12r} = Cob(II)alamin

Braman and Foreback measured the relative amounts of dimethylarsinic acid and methylarsonic acid in various fresh and salt water systems in Florida. Methylarsonic acid, though present, was generally in smaller concentrations than dimethylarsinic acid, possibly because of the greater tendency of methylarsonic acid to oxidize (whereas dimethylarsinic acid is very resistant to oxidation),(28) or possibly because, as shown in the methylation cycle suggested by Wood,(33) the oxidation product of the methylarsines is dimethylarsinic acid which finds its way back into the water system. It appears possible that dimethyarsinic acid and methylarsonic acid could accumulate (from both biological and pesticide runoff sources) to an extent where methylarsine generation and its subsequent deposition in marine organisms might become significant. As stated earlier, very little is known about the rates at which these reactions take place, and thus, the residence time of the slow-to-oxidize dimethylarsinic acid could be appreciable, affording possibly plenty of time for further bacterial reduction to dimethylarsine and subsequent accumulation in aquatic species harvested for food.



A BIOLOGICAL CYCLE FOR ARSENIC

With regard to the biological methylation of metals, Ferguson and Gavis report that the biological advantage, if any, is not known. Ferguson and Gavis as well as Braman and Foreman suggest a possible detoxification advantage in methylation since methylarsonic acid, dimethylarsinic acid, and even the methylarsines (so long as they are in solution) are less toxic generally than the tri- and pentavalent inorganic precursors. Also, in anaerobic environments, the methylation of metals by microorganisms may be more thermodynamically favorable than the synthesis of methane.(7,11)

Ferguson and Gavis(5) state that only aerobic metabolism has been found to yield methylarsines, and that there is not a priori reason why anaerobic synthesis of methylarsines could not also be possible. Wood,(33) on the other hand, referring to the work of McBride and Wolfe (which is also referenced by Ferguson and Gavis), states the methylarsines are produced by anaerobes. Whether aerobically or anaerobically synthesized, Ferguson and Gavis state that methylation is not thermodynamically favored in water and can occur only in the presence of organisms.

(Of all sources referenced here with regard to the methylation of arsenic,(5,8,28,33) all express concern about the extreme toxicity of the methylarsines. However, there is evidence, as cited in the Toxicological Assessment portion of this study, that methylarsines, while in solution or otherwise contained within aquatic organisms, may be of extremely low toxicity, especially in comparison to their gaseous state).

Arsenic is removed from the solution phase by such reactions as adsorption onto clays and coprecipitation into metal ion precipitation. Arsenate, because it is the fully oxidized form of arsenic, is the stable form in aerobic waters, but it may be removed by several mechanisms. For example, that fact that iron oxide has a positive surface charge in most geologic environments has been cited as a reason for the high arsenate adsorption (arsenate is anionic) onto hydrous iron oxides. Arsenate species coprecipitate with or absorb onto hydrous iron oxides. In addition, ferric arsenate is very insoluble.(5)

Arsenite species (trivalent) may be present in surface waters under sufficiently reducing conditions, or if the oxidation to arsenate (pentavalent) is not complete. Arsenous acid species will adsorb onto and/or coprecipitate with iron oxide in a manner similar to that of arsenic (As(+5)) acid.

Aluminum hydroxides and clays also adsorb arsenate species; however, bauxite and silicates are usually only moderately enriched in arsenic. The affinity of arsenite, on the other hand, for clays, and hydroxides other than iron has not been investigated. However, because of the strong affinity of arsenite for sulfur, metal sulfides readily adsorb and coprecipitate arsenite. Goldschmidt and Peters(5) measured up to 3000 mg As/kg of sedimentary pyrite, FeS_2.

Chemistry of Arsenic in Soil

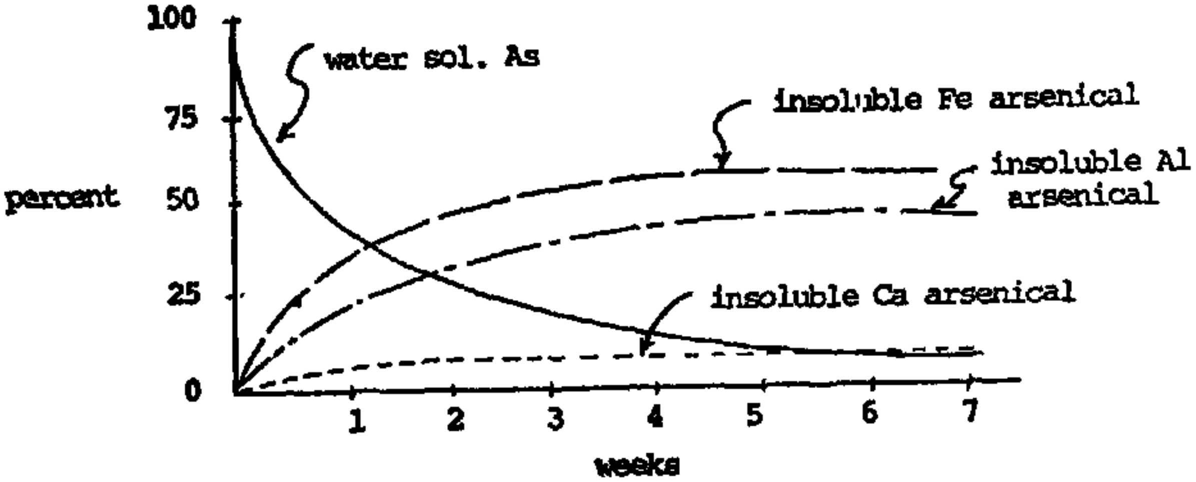
Arsenical compounds arrive in the soil in the form of pesticides, as fallout from smelting operations, from the burning of coal and cotton wastes, and from runoff from mining operations. Arsenic can accumulate in soil to levels that are phytotoxic. Treated soils in North America may contain between 1.8 and 830 ppm As, while untreated soils range from 0.5 to 14.0 ppm As.(15)

When arsenic reaches the soil, it reacts with the soil and soil solution to form compounds of various solubilities.(34) Among the cations that react with arsenic are iron, aluminum, calcium, and magnesium. It also reacts with the hydrous iron and aluminum oxides that cover clay particles in soil. During the reaction process, the chemical equilibrium of arsenic is changed. The amount of arsenic in solution decreases in accordance with such factors as soil pH, available cations, and the amount of organic matter present.(35) Nutrients in the soil, especially phosphorus because of its chemical similarity to arsenic, also affect the rate and degree of arsenic fixation. Phosphorus competes with arsenic both for fixation sites on clay particles and for uptake by plant roots. The degree of phytotoxicity due to arsenic is a function of the total amount of soluble arsenic in the soil.(35,36)

Of the sources of arsenic reaching the soil, arsenical pesticides are the most widely distributed. Arsenic acid (H_3AsO_4) is applied to cotton for leaf desiccation or to vegetation as a general weed killer. The organic arsenicals, methanearsonates and cacodylic acid (dimethylarsinic acid), are selective and general postemergence herbicides, respectively. Other forms in which arsenic may reach the soil are as trivalent salts, pentavalent salts, and, in the case of smelter fallout, simply as arsenic trioxide, As_2O_3. But regardless of the form in which the arsenicals arrive, they are eventually oxidized and/or metabolized to arsenates.(35,37)

The amount of time for an equilibrium condition between soluble and insoluble arsenical species to be reached can be anywhere from several days to many months, depending upon the initial amounts of arsenic introduced to the soil and upon the soil variables listed above (available cations, pH, etc.). Insoluble arsenical species predominate in soils rich in iron, calcium, and aluminum, which means that such soils would tend to exhibit rapid initial reduction of arsenical phytotoxicity, and once equilibrium is reached, arsenical phytotoxicity would be low even though the total amount of arsenic in the soil might be appreciable.(35)

When the initial application of soluble arsenicals is large, the rate of conversion to insoluble forms (on a percentage basis) is slower than when small amounts are applied. But with either large or small initial amounts, the soil decrease of solubles, and the corresponding increase in insoluble salts, typically varies as shown.(36)



That iron-arsenical is shown as being the predominant insoluble compound is purely arbitrary, simply for the sake of illustration. Low volumes of initially water soluble arsenical, in a given soil type, generally decrease more rapidly (e.g., 90 percent conversion to insoluble form within one week) than large volumes (e.g., 50 percent in 24 weeks). In other words, the initial slope of the water soluble curve decreases as the initial (applied) amount of water soluble arsenicals increases; chemical equilibrium is reached more rapidly with lower initial levels of arsenicals.

Arsenic Removal From Soils

Arsenic is removed from soils by three mechanisms: Leaching and runoff; plant uptake; and biological transformation.

Leaching and Runoff

Soluble arsenical compounds can be carried in solution from soil. In the case of leaching, the soluble forms can be carried deeper into the soil profile where they combine with available fixation sites. Leaching of arsenicals to sufficient depths can effectively remove arsenic from the part of the soil where crop roots are likely to absorb it. In the case of runoff, soluble arsenicals are carried away from the soil, and eventually, find their way into ground water or streams and rivers.(38)

Plant Uptake

Plants concentrate arsenic, and with sufficient concentration they die. Plant roots concentrate arsenic at a rate of 10 to 100 times higher than plant tops. Phytotoxicity results from "root pruning"; i.e., arsenic accumulation in root tissues slows or halts root growth while the still-growing plant tops eventually become starved because of insufficient root size. The harvesting of crops and especially the removal of whole plants - crop, stalk, roots, and all - is a mechanism of arsenic removal from soils.(38) Arsenic concentration in plants and its effect on plant growth are discussed in the Toxicological Assessment portion of this report.

Biological Transformation

The biological transformations of arsenicals in soil are similar in many respects to those taking place in water, especially with regard to the formation of highly volatile arsenicals. Soil microorganisms both aerobic and anaerobic, can mediate the transport of arsenic through soil; arsenic removal by volatization results from bacterial formation of arsine (AsH_3), methylarsines (mono-, di-, and trimethylarsine), and other volatile organoarsenic compounds.(37)

In no discussion of the soil chemistry of arsenic surveyed for this study is the possibility mentioned of microbially-mediated reduction of arsenates to arsenites, as has been shown in water systems. Soluble arsenates in soil may undergo chemical reduction to arsenites, but the literature indicates that oxidation to arsenates is more likely in soils, and that the product arsenates are either washed from the soil or locked into insoluble complexes, which, as described above, effectively controls arsenical phytotoxicity. Microbiological metabolic processes therefore act chiefly on organic arsenicals, mainly methanearsonic acids (which include the herbicides DSMA and MSMA) and dimethylarsinic acid (the herbicide, cacodylic acid).

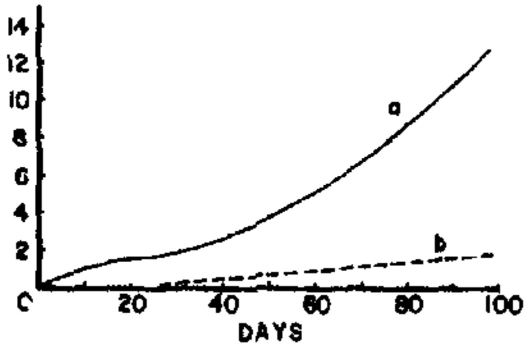
In aerobic soils, the organic arsenicals will, in time, be oxidized, either chemically or as a result of biological processes, to carbon dioxide and arsenate. It is also possible in aerobic soils for organic arsenicals to be reduced to volatile organo-arsenical compounds in the same manner as described in the section of this study dealing with the chemistry of arsenic in water; namely, organo-arsenicals are reduced and methylated to mono-, di-, and trimethylarsines, as well as to inorganic arsine and to other volatile organo-arsenicals.(37)

As would be expected, it is under the anaerobic conditions where the largest portion of nonvolatile organo-arsenicals (specifically, cacodylic acid) are converted to volatile forms instead of being oxidized. In a study by Woolson and Kearney(37) of the degradation of cacodylic acid in three types of soils, an average of 61 percent of applied cacodylic acid was converted under anaerobic conditions to a volatile organo-arsenical within a 24-week period, whereas under aerobic conditions, 35 percent was made volatile and 41 percent oxidized into CO_2 and arsenate in the same period. (Under the anaerobic conditions, none of the cacodylic acid was oxidized to CO_2 and arsenate).

The reactions of the methanearsonic acids in soil are similar to those of cacodylic acid - metabolism to volatile compounds in both aerobic and anaerobic soils, and oxidation (and off-gasing of CO_2) in aerobic soils.(38)

Dimethylarsine is a common volatile arsenical, and according to Woolson and Kearney,(37) it is so unstable that it may be oxidized back into cacodylic acid by its contact with air and return to the soil to either repeat the cycle or to by oxidized and finally fixed into the soil. The ultimate environmental fate of arsenic in soil appears to be the formation of inorganic arsenate which becomes bound as insoluble compounds in the soil.

Oxidation of cacodylic acid and methanearsonic acids can, however, be part of biologically-mediated metabolic processes — at least in aerobic soils. Woolson and Kearney found such evidence in measuring the evolution of CO_2 from soil which had on two occasions received cacodylic acid; on the second occasion the adapted microbiological population metabolized the cacodylic acid much more readily than in fresh soil: 13-percent release of the initial carbon (^{14}C) after 98 days versus only 2 percent after the same period in fresh soil. The diagram below illustrates the difference.(37)



EVOLUTION OF $^{14}CO_2$ FROM AN ADAPTED (a) AND A NON-ADAPTED (b) SOIL TREATED WITH CACODYLIC ACID

Effects of Phosphorus (36)

Increasing phosphorus levels in nutrient solutions containing sufficient arsenic to reduce growth has been shown to cause less arsenic to accumulate in plants and to improve plant growth where it would otherwise be slowed by the presence of arsenic. This affect, however, does not always hold true. In one study where soil levels of Al and Fe were low, phosphorus seemed to magnify the phytotoxicity of arsenic, possibly because the phosphorus combined with the few fixation sites available so that arsenic did not form insoluble compounds which would have taken it out of solution.

Since phosphorus is an important ingredient in fertilizers, it could play a part in the phytotoxicity of the total arsenic in a given soil situation. If the soil has a high potential for fixation of these two chemically similar elements, the available phosphorus in solution will be preferentially absorbed by plants, and the arsenic will not be as harmful. In soils with a low potential for fixation, especially with respect to Fe and Al, phosphorus will be predominatly fixed while arsenic will remain available for plant uptake, and, hence, phytotoxicity.

In general, plant content of arsenic and phosphorus appears to be a function of their soil availability. Soils which are high in accumulated arsenic (highly insoluble forms associated with Fe and Al, mainly in clay particles) are affected by the addition of phosphorus. Phosphorus can increase the amount of soluble arsenate in soil and, thus, hasten the leaching of arsenic from the top soil. Thus, in soils containing initially high levels of insoluble arsenic, high phosphate fertilizers may provide a mechanism for moving some of the toxic, more soluble arsenic deeper into the soil profile.

SECTION IV

ARSENIC PRODUCTION AND USES

Table 1 summarizes arsenic supply and use volumes for those years between 1968 and 1974 for which data were available. Though there is only one domestic supplier of arsenic trioxide, production information is unavailable. The supply information in the Table shows considerable variation between data sources. With regard to exports, approximately 25 percent of the domestic production was exported in 1974, according to a spokesman for ASARCO, the single arsenic producer.(39)

The major uses of arsenic are:

- Pesticides
  - Insecticides
  - Herbicides
  - Fungicides
- Wood Preservatives
- Feed Additives
- Glass Manufacture
- Nonferrous Alloying

Data Collection and Use Trends

Pesticides

Arsenical pesticides account for less than 3 percent of the total pesticide market, and their share is decreasing as a result of cancellation of pesticide registrations(40) and because of the increasing concern of the Occupational Safety and Health Administration for the health of arsenic workers - compliance with exposure standards, both current and proposed, has been named as a factor in the decreased use of inorganic arsenicals.

Lead and calcium arsenate and Paris green account for virtually all of the arsenical insecticides currently used. The arsenical herbicides (including defoliants and desiccants) are the methanearsonates, cacodylic acid, and arsenic

TABLE I

ARSENIC SUPPLY AND USE
1968 - 1974
(Kkg As)

	1968	1969	1970	1971	1972	1973	1974
White Arsenic Supply - Total	25,460(a) 21,600(f)						18,800(d)
Domestic Production	7,260(a) 5,540(f)	NA	9,550(b)	NA	NA	NA	8,193(c) 12,250(d)
Imports (Metallic and Oxide)	18,200(a) 13,500(e) 17,900(f)	12,700(e)	13,200(e)	12,250(e)	9,880(e)	8,500(e)	9,550(d) 5,370(e)
Exports	NA*	NA	NA	NA	NA	NA	3,000(d)
Pesticides - Total	17,700(a) 16,250(f)						12,920(d)
Lead Arsenate (n)	465	750	575	406	494	NA	NA
Calcium Arsenate (n)	340	364	496	421	300	NA	NA
Methanearsonic Acid Salts	NA	NA	4,820(h)	3,900(h)	4,860(h)	3,965(g)	4,290(g)
Cacodylic Acid(p)	NA	NA	NA	NA	NA	NA	NA
Arsenic Acid	724(i)	969(i)	1,212(i)	1,460(i)	2,070(j)	2,700(j)	3,300(j)
Wood Preservatives - Total	363(a) 637	836	847	1.099	1.141	1,358	1,400(d)
Chromated Copper Arsenate (CCA) (k)	346	504	650	940	1,000	1,234	NA
Fluor Chrome Arsenate Phenol (FCAP) (k)	291	332	197	159	141	124	NA
Feed Additives(l)	349	370	397	392	409	400	409(d)
Glass Manufacture	3,725(f) 5,000(a) 2,800(b)	3,500(m)	3,160(m)	2,820(m) 2,045(b)	2,480(m)	2,140(m)	1,805(d)
Nonferrous Alloying	363(a) 636(f)	363(n)	372(n)	436(n)	541(n)	529(n)	541(n) 1,272(d)
Miscellaneous	2,000(a)	1,650(o)	1,700(o)	1,575(o)	619(o)	523(o)	317 330(d)

*NA = not available

NOTES:

(a) Data from National Inventory of Sources and Emissions: Arsenic - 1968.

(b) Data from Recommended Methods of Reduction, Neutralization, Recovery, or Disposal of Hazardous Waste.[1]

(c) Data from Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. February 1975. EPA 440/1-75/032-b.

(d) Based on information supplied by the American Smelting and Refining Company to the Occupational Safety and Health Administration with regard to the proposed standard for exposure to inorganic arsenic.[39]

(e) From the Arsenic section of the Commodity Data Summaries 1975[18] (and personal communication with Gertrude Greenspoon, BOM)

(f) Paone, James. Arsenic. In: Mineral Facts and Problems, 1970 edition. U.S. Department of the Interior, Bureau of Mines, pp. 479–487.[17]

(g) Personal communication with a spokesman for the Ansul Company.

(h) Based on data from the Pesticide Review 1973,[43] and from Farmers' Use of Pesticides in 1971 . . . Quantities.[49]

(i) Based on assumed linear growth between 1966 and 1971, two years for which data were available – Farmers' Use of Pesticides in 1971 . . . Quantities.[49]

(j) Projection of 1975 demand supplied by arsenic acid producers – assumed linear relation 1971 through 1975.

(k) Data supplied by the American Wood-Preservers' Association.[19]

(l) Feed additive use in 1973 was inferred from information supplied by the National Agricultural Chemical Association – years 1968 through 1972 are based on broiler production for those years, adjusted to 1973 broiler production.

(m) Based on assumed linear decrease between average of figures for 1968 and Asarco data for 1974.[18]

(n) Based on 90 percent of metallic arsenic imports as reported by Bureau of Mines. (No metallic arsenic produced in the U.S. between 1968 and 1974, at which time Asarco started producing it.)[18]

(o) Includes such uses as animal dips and paint pigments and additives which no longer contain arsenic;[63,65] from 1969 to 1971, basis is 10 percent of imports of white arsenic; 1972 through 1974 based on 5 percent of white arsenic imports.[18]

(p) Cacodylic acid is a major arsenical herbicide, but no production or use data are available.

acid; other arsenical herbicides such as sodium arsenite and mixtures containing arsenic trioxide were in use in the last decade, but if they are still in use, no producers or production information were uncovered in this study. The EPA Compendium of Registered Pesticides lists several dozen arsenical herbicides and insecticides, but the ones listed above are the only ones finding any use today. Similarly for arsenical fungicides, several are listed but only one - 10,10'-oxybisphenoxarsine - is in use (as an additive to flexible vinyl plastic formulations), and production information is not available from the single producer.

Most of the pesticide data in the Table is from Department of Agriculture sources, and part of it has been supplied by producers. Total arsenical pesticide production is decreasing, but the high figure of 17,700 kkg of elemental arsenic used in pesticides in 1968 probably was a result of military use of cacodylic acid as a defoliant (agent BLUE) in Vietnam.(41,42) Use of cacodylic acid in Vietnam probably reached a peak around 1970, but no data are available to substantiate this. Production of calcium and lead arsenate decreased between 1968 and 1972, but "domestic disappearance" data for the same period (which takes account of imports, exports, and producer year-end inventories) shows no trend. The lead arsenate and calcium arsenate data in the Table is based on domestic disappearance since it better reflects demand than does the production data.

The use of arsenic acid has increased dramatically during the last decade. Arsenic acid is used almost exclusively as a cotton harvest aid (specifically, as a desiccant) in Texas and Oklahoma where the so-called "dry-land" cotton is grown. Cacodylic acid is also used as a cotton harvest aid, largely in the nine other cotton-producing states.

Wood Preservatives

The two main arsenical wood preservatives are chromated copper arsenate (CCA) and fluor chrome arsenate phenol (FCAP). Small amounts of ammoniacal copper arsenate (ACA) are also being used by a wood-treating plant on the west coast. CCA presently accounts for about 90 percent of the arsenical wood preservative use,(44) since once it becomes bound to the wood fibers it is impervious to leaching, as opposed to the other water-borne wood preservatives. Data were supplied by the American Wood-Preservers' Association and by the producers of arsenical wood preservatives. Use of CCA is increasing; FCAP is decreasing.(45)

Feed Additives

Arsenical feed additives are used in the feed of poultry and swine to increase growth rate and feed efficiency, and, in some instances, to control poultry disease. Data were available only for the years 1973 and 1974; data for previous years was derived on the basis of broiler production for the years 1968 through 1973, assuming a constant ratio of arsenic to broilers for each year. According to an FDA source,(46) arsenical feed additives are proportional in total volume to broiler production, and will grow or decline accordingly.

Glass Manufacture

Data on the use of arsenic in the manufacture of glass is conflicting. Of the glass manufacturing specialists contacted, one stated emphatically that arsenic is no longer used in glass because of the handling hazards and because of problems in disposing of arsenic containers. Another specialist said arsenic was still used, but only in specialty and "art" glass. The use of arsenic in glass is definitely decreasing.

Nonferrous Alloying

Arsenic is used in lead, brass, and copper alloys to improve certain metallurgical properties. The apparent increase in this use shown in the Table is based on increased imports of metallic arsenic as reported by the Bureau of Mines. One of the major alloying uses is in lead shot where arsenic increases the hardness and sphericity of the shot. However, the use of lead shot may be curtailed by the Bureau of Sport Fisheries and Wildlife because of evidence that ducks and other birds are being lead-poisoned from eating the shot; an iron-based shot will likely be the alternative.(47)

Miscellaneous

The miscellaneous uses of arsenic include, or have included, the following during the last decade:

- animal dips, paint pigments and additives, and leather tanning chemicals - all of which no longer use arsenic
- pharmaceuticals - human use of arsenical pharmaceuticals has effectively ceased, but they are still used in verterinary application other than as feed additives
- electronics - semiconductor uses in diodes, transistors, lasers and infrared devices, plus increasing use in light-emitting diodes for digital readout.

The remainder of this section is a detailed discussion of the uses of arsenic, the enviornmental emissions resulting from these uses, and alternative materials for these uses.

Pesticides

Herbicides and insecticides are the two main pesticides. Other pesticides include fungicides, rodenticides, miticides, acarcides, and nematocides. At the present time, more that 80 percent of pesticides are organic chemicals, a substantial change from the 1940's when pesticide chemicals were almost entirely inorganic, with insecticides, the largest part of the pre-war pesticide market, consisting largely of lead arsenate and calcium arsenate.

Insecticides

Volume III of the EPA Compendium of Registered Pesticides lists the following arsenical insecticides:

Arsenic Pentoxide
Arsenic Trioxide
Basic Copper Arsenate
Cacodylic Acid
Calcium Arsenate
Copper Arsenate
Lead Arsenate
Paris Green (copper acetoarsenite)
Potassium Arsenite
Sodium Arsenate
Sodium Arsenite
Sodium Pyroarsenate

Two of these compounds, sodium arsenite and potassium arsenite, are listed in the Compendium as acarcides (tick killers) used in animal dips. As such, they are discussed separately in the Animal Dip section of this report.

	Cotton	Tobacco	Peanuts	"Other Field Crops"	Irish Potatoes	"Other Vegetables"	Citrus	Apples	"All Other Fruits and Nuts"	Nursery and Green House Crops	TOTAL
Inorganic Insecticides* (kkg)	31	44	8	0.9	1.4	90	154	842	220	0.5	1,383*
Total Insecticides (kkg)	33,348	1,883	2,724	1,039	1,313	3,861	19,605	4,782	8,417	300	97,717
% Inorganic of Total	0.094	2.3	0.28	0.088	1.0	2.3	0.78	17.6	2.6	0.15	1.41

*Figure includes cryolite (115 kkg) and sodium fluosilicate (7.3 kkg); remainder is arsenical.[12]

(That the total inorganic insecticide use on crops, 1,383 kkg, is less than half of the reported production of lead arsenate and calcium arsenate for the same year is accounted for by the uses of lead arsenate and calcium arsenate in non-crop uses by government, industry, and homeowners.)

The only organic arsenical insecticides listed in the EPA Compendium are cacodylic acid and paris green. Cacodylic acid is not used on crops and paris green is used exclusively as a mosquito larvacide. Thus, all arsenical insecticides used on crops are included under the heading "Inorganic Insecticides in the above table. The largest use of inorganics is on apples (17.6% of all insecticides used on apples) followed by "All other fruits and nuts"* (2.6%).

Thus, arsenicals - except in the case of apples - account for only a small part of the total insecticides used on crops in 1971 (1.4%), and the downward trend noted between 1966 and 1971 in inorganic seems to be continuing.(50)

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*grapes, avocados, figs, blackberries, blueberries, boysenberries, currants, gooseberries, loganberries, raspberries, strawberries, almonds, filberts, pecans, walnuts, olives, tung nuts.

Arsenic pentoxide is used to protect wood against termites; it is discussed in the Wood Preservative section.

Prior to WW II, lead and calcium arsenate were the "backbone of the pesticide industry". These two compounds significantly decreased in use since 1940.(48)

	1940	1960	1965	1967	1968
			(1000 kkg)		
lead arsenate	34.1	4.5	3.2	2.7	4.1
calcium arsenate	22.7	3.2	1.8	0.9	1.4

The compounds are no longer the backbone of the pesticide industry, but they are the backbone of the arsenical insecticide industry, with lead arsenate carrying the major portion of the burden.

	1967	1968	1969	1970	1971	1972
				(kkg)		
lead arsenate	2,700	4,100	4,170	1,880	2,800	2,530
calcium arsenate	930	1,540	527	522	427	(w)

(w) ≅ data withheld to avoid disclosure

Agricultural Economic Report No. 252, Farmers' Use of Pesticides in 1971 ... Quantities,(49) states that inorganic insecticide use in 1966 and 1971 was "relatively insignificant"; it dropped from 2,630 metric tons in 1966 to 1,450 metric tons in 1971, "down from 4 percent to less than 2 percent of all insecticides used".

The same publication lists the crops and amounts of insecticides used in 1971. Under the heading "inorganic insecticides" (unspecified), ten crops are listed.

Herbicides

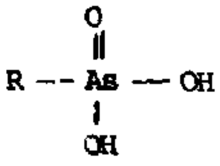
Arsenical herbicides used today are largely of the organic variety. Inorganic arsenicals are rarely used any more, with the notable exception of arsenic acid used as a cotton harvest aid. In the past, arsenical herbicides were usually of the trivalent form, which is usually more water soluble and thus more easily absorbed by plant tissues, either through the roots or directly through the leaves.

Sodium arsenite was the standard weed killer for most of this century until about 1960; that is, when more effective and more highly selective organic herbicides became available.(31)

Arsenic trioxide, which is a relatively insoluble trivalent arsenic compound, is used in soil sterilization. Its disadvantages include high dosage rates (400 to 800 pounds per acre are required) and soil residues, which remain for many years even though actual soil sterilization may be effective for only a year or so. Non-arsenical herbicides are effective at dosages on the order of only several pounds per acre.(31)

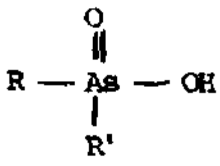
Arsenicals kill plants via inhibition of enzymes containing sulfhydryl groups. Protein precipitation within plant cells is a consequence of high arsenical concentrations. Arsenicals generally are not specific in their herbicidal action.(31)

The organic arsenicals are classed as either arsonic or arsinic acids. The basic structural formulas are:



$$\begin{array}{c} O \\ \| \\ R - As - OH \\ | \\ OH \end{array}$$

Arsonic Acid



$$\begin{array}{c} O \\ \| \\ R - As - OH \\ | \\ R' \end{array}$$

Arsinic Acid

where R and R' correspond to a variety of organic groups, cacodylic acid, which is dimethylarsinic acid, is based on arsinic acid with methyl groups in place of R and R'. The salts of arsonic acid are disodium methanearsonic acid (DSMA), monosodium acid methanearsonate (MSMA), amine methanearsonate (AMA), and calcium acid methanearsonate (CMA).(31)

Cacodylic acid and the arsonic acids are pentavalent arsenicals. They are generally less toxic to animals than organic trivalent arsenicals, and they are considerably less toxic than inorganic arsenicals. (See Table 11 which shows the relative toxicities of various arsenical compounds.) The methanearsonates and cacodylates are classed as contact herbicides, which means they don't have to be absorbed through the roots to be effective.

The arsenical herbicides listed in Volume I of the EPA Compendium of Registered Pesticides are:

Arsenic Acid (orthoarsenic acid)
Arsenic Trioxide
Arsenous Oxide
Basic Copper Arsenate
Cacodylic Acid
Calcium Acid Methanearsonate
Calcium Arsenate and Tricalcium Arsenate
Calcium Propanearsonate
Diammonium Methanearsonate
Disodium Methanearsonate and Methanearsonic Acid
Lead Arsenate and Standard Lead Arsenate
Monosodium Acid Methanearsonate and Monammonium Methanearsonate
Dodecylammonium Methanearsonate and Octylammonium Methanearsonate
Sodium Arsenite

The underlined names are the ones for which information has been included in the Compendium - the other items are merely listed in the index and further data will be incorporated at some future time. The existing write-ups include registered uses, tolerances (in soil and on agricultural products), and limitations (eg., State prohibitions, part of plant life-cycle when most effective).

The Criteria and Evaluation Branch of the Office of Pesticide Programs has compiled a list of arsenical herbicides and a preliminary list of non-arsenical alternatives registered for the same uses as the arsenicals. This compilation and search for non-arsenical alternatives is part of an on-going study at EPA. The list of alternatives will be trimmed as EPA gathers information on the economics and characteristics of each alternative, such as cost and availability of the alternative, efficiency within different climates and on various soil types, and information on the methods of application (which could entail a large capital outlay for new equipment, if the alternative material must be applied differently from the arsenical).

The 1975 Weed Control Manual, included in the February 1975 edition of Agri-Fieldman,(51) lists the currently available herbicide products and their manufacturers. The arsenical compounds used in these products are:

Monosodium Acid Methanearsonate (MSMA)
Disodium Methanearsonate (DSMA)
Cacodylic Acid
Amine Methanearsonate (AMA)
Calcium Acid Methanearsonate
Dodecylammonium Methanearsonate
Oxtylammonium Methanearsonate

All of these compounds are listed in the EPA Compendium; only the first three are listed in the table compiled by the Criteria and Evaluation Branch of the Office of Pesticide Programs. Cacodylic acid, DSMA, and MSMA constitute virtually the entire organic arsenical herbicide market.

Arsenic acid, because of its high water solubility, is a very potent herbicide. During the past decade, it has increased dramatically in use as a cotton plant desiccant; i.e., a harvest aid which is applied prior to machine picking.

The Farm Chemicals Handbook(52) lists four producers of arsenic acid used in cotton desiccation. In checking with these producers, it was found that one no longer produces arsenic acid, and that two produce it for in-house uses only, such as the production of lead and calcium arsenates. Two producers, both located in Texas, supply virtually all of the arsenic acid used in cotton production. They are the Bryan, Texas, Division of the Pennwalt Company, and Voluntary Purchasing Group (VPG) of Bonham, Texas.(53)

In the Texas-Oklahoma area, 85 percent of the cotton is "dry land" cotton which yields 1/4 to 1/2 bale per acre, and 15 percent is spindle cotton which yields 1 to 2 bales per acre. (Spindle cotton is more expensive to raise since it requires irrigation and many doses of insecticides.) The dry land cotton is machine picked ("stripped") at a cost on the order of 10 percent of the cost of manual picking. Industry spokesmen claim that many cotton growers would have to go out of business if arsenic acid becomes unavailable for desiccation purposes. The non-arsenical alternative is paraquat, but this is allegedly not as effective as arsenic acid, and it is more expensive per application.(53,54)

Demand for arsenic acid is increasing. In 1966, the amount of arsenic acid used in cotton desiccation was 443 metric tons, while by 1971 it had increased to 2,750 metric tons.(49) In 1975, arsenic acid consumption is estimated to be on the order of 7,460 metric tons.(53)

The following table shows the use-distribution of arsenical herbicides on crops (1971 data):(49)

	Cotton	Sorghum	Rice	Soybeans	Pasture and Rangeland	Citrus	All Other Fruits and Nuts	Summer Fallow	Total
Organic Arsenical (kkg)	3,440	84	1.4	22	0.45	3.2	10	0.45	3,550
Total Herbicides (kkg)	51,200	5,250	3,620	16,600	18,600	30,500	9,900	715	167,000
As % of Total	6.7	1.6	0.038	0.13	0.0024	0.01	0.1	0.063	2.1

Note that arsenical herbicides used account for only about 2 percent of total herbicide use on crops, and that cotton is the most arsenically-dependent crop.

Fungicides

The bulk of arsenical fungicides are used as wood preservatives. There is one arsenical fungicide, however, which is used to control fungus attack of vinyl plastics. It is 10,10'-oxybisphenoxarsine, marketed as Vinyzene (in about five different formulations) by the Ventron Corporation of Beverly, Massachusetts.

The Vinyzene formulations contain either 1 or 2 percent of the active fungicide 10,10'-oxybisphenoxarsine (10,10'-OBPA). The empirical formula for 10,10'-OBPA is $C_{24}H_{16}As_2O_3$; it is 30 percent As and 40 percent As_2O_3.

Fungicides such as Vinyzene are used in plasticized polyvinylchloride products which are exposed in use to humid environments. The PVC resin itself is not normally attacked by fungi; it is the plasticizers which need protection from fungal attack. Rigid vinyl products such as plumbing pipe do not require fungicide additives. Typical calendered and flexible vinyl products in which fungicides might be used include shower curtains, hospital sheeting, upholstery, electrical cable jackets, refrigerator gaskets, wall coverings, automobile landau tops, other auto parts, boat covers, awnings and tarpaulins, pond and swimming pool liners, and plastic pants for babies.

In the case of the arsenical Vinyzene, the common formulations contain 1 percent 10,10'-OBPA, with 2 percent formulations used for very humid outdoor applications. The active ingredient is normally dispersed in epoxidized soybean oil, a plasticizer, for use by plastic molders at about 3 parts per hundred of resin (phr). Dispersions in other plasticizers such as dioctylphthalate or diisodecylphthalate, and formulations using solvents such as methyl ethyl ketone or mineral spirits, are produced to a lesser extent.

The use of Vinyzene has grown very rapidly over the past ten years, but it still accounts for only a very tiny fraction (0.02 percent) of all the white arsenic used in the U.S.:

Year	Vinyzene Formulations, kkg/year	10,10'-OBPA, kkg/year	Arsenic as As_2O_3, kkg/year
1965	30	0.3	0.1
1966	40	0.4	0.2
1967	100	1.0	0.4
1968	180	1.8	0.7
1969	340	3.4	1.3
1970	380	3.8	1.5
1971	600	6.0	2.4
1972	850	8.5	3.3
1973	1,030	10.3	4.1
1974	1,390	13.9	5.5

Although Vinyzene has more than 50 percent of the total fungicide (for plastics) market, the overall market penetration of all fungicides is only about 10 percent. Hence, even if the entire potential market were captured by Vinyzene, the quantity of 10,10'-ORPA would be only 280 metric tons per year, with an As_2O_3 equivalent of only 110 metric tons per year.(55)

At the standard use rate of 3 phr for a 1 or 2 percent formulation, the active ingredient 10,10'-OBPA is in the vinyl product at a concentration of 300 or 600 ppm. The tight structure of the molecule makes it extremely stable, and it has no discernable vapor pressure. Skin irritation and sensitivity tests gave acceptably low results. The active ingredient was not extracted from PVC film by water, perspiration, or skin oil; and none was volatilized up to 250°C. Since much of the PVC products in which Vinyzene is an ingredient enters the municipal solid waste stream, a significant portion is incinerated, whereupon As_2O_3 is emitted to the atmosphere. The quantity involved, however, is extremely small compared to other As_2O_3 atmospheric emissions.

The large market share of all vinyl fungicides enjoyed by Vinyzene is in part due to its 10 to 15 percent lower cost than competitive materials. The substitutes include barium metaborate and the following organics:

N-(trichloromethylthio)phthalimide
2-n-octyl-4-isothiazolin-3-one
N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide
Triphenylin nonylphenoxide
diphenylstibine 2-ethylhexoate

Wood Preservatives

The American Wood Preservers' Association lists three arsenical wood preservatives:

Chromated Copper Arsenate	(CCA)	(Types A, B, and C)
Fluor Chrome Arsenate Phenol	(FCAP)	
Ammoniacal Copper Arsenite	(ACA)	

These compounds are classed as water-borne preservatives. The standards established by the AWPA call for the following compositions (tolerances not given here):(56)

Chromated Copper Arsenate

	Type A	Type B	Type C
Hexavalent chromium as CrO_3	65.6%	35.3%	47.5%
Copper As CuO	18.1%	19.6%	18.5%
Arsenic as As_2O_5	16.4%	45.1%	34.0%

Fluor Chrome Arsenate Phenol

	Type B
Fluoride as F	22%
Hexavalent chromium as CrO_3	37%
Arsenic as As_2O_5	25%
Dinitrophenol	16%

Ammoniacal Copper Arsenite

Copper as CuO	49.8%
Arsenic as As_2O_5	50.2%

The trade names of the arsenical products are:

Chemonite	ACA
Greensalt	CCA Type A
Langwood	
Boliden CCA	CCA Type B
Koppers CCA-B	
Osmose K33	
Chrome-Ar-Cu (CAC)	CCA Type C
Wolman CCA	
Wolmenac CCA	
Osmosalts (Osmosar)	FCAP
Tanalith	
Wolman Salts FCAP	
Wolman Salts FMP	

Wood treated with preservatives is used in these applications:(45)

	Type of Treatment (1973)	
	Arsenical	Other
Poles	~ 2%	97%
Crossties	-	99%
Lumber and timbers	47%	46%

	Arsenical	Other
Fence posts	4%	96%
Piling	-	97%
Switchties	-	>99%
Crossarms	-	99%
Plywood	42%	58%

The arsenicals used in these applications are mainly chromated copper arsenate and fluor chrome arsenate phenol; ammoniacal copper arsenite accounts only for 9 percent of the arsenical usage in plywood preservation, 5 percent of the lumber and timber, and no other significant usage. Thus, CCA and FCAP are effectively the only arsenical preservatives listed by the American Wood Preservers' Association, and these two compounds are used only in poles (~2%), lumber and timbers (45%), fence posts (4%), and plywood (~38%).

Consumption of solid preservatives (as opposed to liquid preservatives - creosote and petroleum - which are the mainstays of the wood preservative industry) has followed a pattern where fluor chrome arsenate phenol is gradually phasing out, while chromated copper arsenate is growing in use.(57)

Solid Preservatives (45)
(kkg)

	Chromated Copper Arsenate	Fluor Chrome Arsenate Phenol	Pentachlorophenol	Total Preservatives
1965	-	2,610	9,200	14,300
1966	-	3,140	11,800	17,600
1967	1,060	2,430	11,300	16,350
1968	1,460	1,800	12,000	17,900
1969	2,120	2.060	11,600	18,050
1970	2,740	1,220	12,900	17,800
1971	3,960	987	14,600	20,500
1972	4,430	870	16,600	23,200
1973	5,320	767	17,700	25,300

Thus, in 1973, chromated copper arsenate accounted for 21 percent of the total solid preservatives consumed and fluor chrome arsenate phenol accounted for 3 percent.

Looking at the total preservative picture (liquids and solids), 254,443,000 cubic feet of wood were preserved in 1973, of which chromated copper arsenate accounted for 12 percent (29,414,000 ft^3), fluor chrome arsenate phenol accounted for 1.4 percent (3,604,000 ft^3), and ammoniacal copper arsenite and all other arsenical wood preservatives (see below) accounted for even less.

The wood preservatives discussed above are used to protect wood against fungus attack and microbially-mediated rot. Insects, especially termites, are also a consideration in wood preservation. The EPA Office of Pesticides Programs has compiled a list of arsenical insecticides used as wood preservatives. They are:

Ammonium arsenite
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Sodium pyroarsenite
Wolman salts (fluor chrome arsenate phenol)

The reason for the absence of CCA (chromated copper arsenate) from this list is not known. The registered alternatives for these compounds are given as creosote and pentachlorophenol.

EPA has also compiled a list of arsenical fungicides used as "industrial wood preservatives". They are:

Arsenic acid
Arsenic trioxide mixtures
Arsenic pentoxide mixtures
Disodium arsenate mixture
Sodium arsenate mixture
Ammonium arsenite mixtures

The use of these compounds is extremely limited, if indeed they are used at all any more.

Feed Additives

The arsenical feed additives are:

Arsanilic acid
Roxarsone (3-nitro-4-hydroxyphenylarsonic acid)
Carbarsone (p-ureidobenzenearsonic acid)
Nitarsone (4-nitrophenylarsonic acid)

The purposes of arsenical feed additives are disease prevention and control, and to improve feed efficiency and weight gain. Arsenicals are restricted almost entirely to poultry, though some are used for swine.

Carbonsome is used in turkey feed only; its function is to prevent or control histomoniasis (blackhead), a protozoan parasite disease of turkeys. It is sold in combination with colloidal aluminum silicates containing 37.5 percent Carbarsone (Carb-O-Sep), or in combination with antibiotics. Carbarsone is also used to prevent and control coccidiosis, a common poultry disease. In combination with Bacitracin, Carbarsone also increases weight gain in turkeys.(58)

Nitarsone is used to prevent and control blackhead in chicken and turkeys. In combination with various antibiotics, Nitarsone will also stimulate growth and improve feed efficiency.(58)

Roxarsone promotes growth and improves feed efficiency and pigmentation in chickens and turkeys. It also increases egg production in laying chickens. In combination with antibiotics, Roxarsone prevents and controls various chicken and turkey diseases, and promotes growth and improves feed efficiency.(58)

Arsanilic acid (or sodium arsanilate, the water-soluble salt of arsanilic acid) increases weight gain and improves feed efficiency in chickens and turkeys; it also increases egg production and feed efficiency in laying chickens and prevents coccidiosis in both layers and nonlayers. In combination with various antibiotics, arsanilic acid prevents and controls certain diseases, as well as improves weight gain and feed efficiency.(58)

In swine, arsanilic acid (often in its water soluble form - sodium arsanilate) increases weight gain and feed efficiency. In combination with antibiotics is prevents, treats, or controls various internal diseases such as salmonella, and dysentary.

All commercial combinations of antibiotics with arsenical feed additives must be approved by the FDA. Federal law requires a 5-day withdrawal period before slaughter for poultry.(46,58) Arsenicals tend to accumulate in poultry livers, but the 5-day withdrawal period is sufficient for liver levels to return to normal, non-arsenical levels.(59)

Names of producers of arsenical feed additives are listed in the Feed Additive Compendium.(58)

Nonferrous Arsenical Alloys

Arsenic in small amounts can influence the mechanical and chemical properties of copper, lead, and brass.

Copper

Arsenic in copper increases corrosion and erosion resistance, raises annealing temperature, and possibly serves as a deoxidizer. Arsenical copper, as it is called, contains up to 0.5 percent arsenic. The higher annealing temperature of arsenical copper allows the material to retain its strength after soldering; thus, automobile radiators and other such copper parts fabricated by soldering are likely to contain arsenic.(60)

Arsenical copper has also been used in the manufacture of boiler tubes used in power plants in the central U.S. where water conditions are relatively mild. This use has, however, diminished in recent years because of high cost compared with Muntz metal and inhibited admiralty.(60)

Lead

The most widely known use of arsenic in lead is probably in the manufacture of lead shot. Arsenic in amounts of up to 1 percent alters the characteristics of molten lead so that the shot produced is of a more spherical shape.

Lead shot is likely to be banned on flyways because of the poisoning of ducks who eat the shot (lead poisoning). Iron-lead alloy will likely replace the lead-arsenic alloy now used. The Bureau of Sport Fisheries and Wildlife will be the banning agency. An estimated 1,145 kkg of arsenic is used annually in the production of lead shot.(39,47)

In engine bearings of the type used in automobiles and trucks, additions of up to 3 percent arsenic to the usual lead-tin-antimony babbitt improves bearing life significantly; it produces an increase in both strength and endurance limit, especially at high engine temperatures, and it probably also inhibits the bearing corrosion which is common in engines under adverse service conditions.(60)

In the electrolytic deposition of copper from solutions containing chlorides and nitrates, the anodes have been made from lead-antimony alloys containing from 0.6 to 6.8 percent arsenic. The arsenic reduces the anode solubility.(60)

Lead-acid storage batteries typically contain antimony in the lead as a hardener, especially for the posts and plates. Arsenic is used in amounts up to 0.5 percent, also for hardening, and to otherwise extend battery life. Arsenical lead for batteries is purchased as such from lead suppliers.(61)

Cable sheathing must be strong and corrosion resistant. Chemical lead, 1 percent antimonial lead, and arsenical lead alloys have been used in cable sheathing made of lead.

Brass

Arsenic in brass inhibits dezincification and the resultant season cracking, corrosion processes whereby zinc dissolves out of brass thus making it brittle and spongy.

Arsenic usage in nonferrous alloys was estimated to have been 360 kkg in 1968.(9) Bureau of Mines data(18) show a general increase in metallic arsenic imports between 1970 and 1974, and since the main use of metallic arsenic is in nonferrous alloying, then such consumption could possibly be increasing.

	1970	1971	1972	1973	1974
Metallic As Imports (kkg)	415	486	600	583	590

No metallic arsenic was produced in the U.S. during this period.

Glass

Arsenic is not widely used in glass any more, and when it is, it is classed as a "minor ingredient" - i.e., measured on the order of ounces per ton.

Arsenic in glass serves two manufacturing purposes: (1) as an oxidizing agent, and (2) as a fining agent. As an oxidizing agent, arsenic in the form of sodium arsenate oxidizes iron (FeO oxidized to Fe_2O_3) so that it will not discolor the glass. This oxidizing operation can also be performed using non-arsenical sulfate or sodium nitrate (niter) - in fact, in most instances these days, the non-arsenical alternatives are used, especially since they are efficient in the oxidation of other possible impurities such as carbon (which can be oxidized by niter).(62)

Fining is the removal of bubbles. As a fining agent, arsenic trioxide and niter are mixed into the glass. The arsenic trioxide is oxidized to arsenic pentoxide which, by thermal decomposition, releases oxygen bubbles which rise to the surface carrying with them bubbles of other gases in the glass. Non-arsenical sulfates are mostly used for fining these days.(62)

Sulfates are used for oxidizing and fining to such an extent these days that arsenic use has dwindled to almost nothing. The types of glass where arsenic would most likely be used (for fining and oxidizing) are flat glass, container glass, and "art glass". In virtually all forms of these glasses, however, non-arsenical sulfates are likely used nowadays, and in the cases where arsenic is still used, a possible alternative (which has been used) is antimony oxide.(62)

The oxidation of Fe in glass is one step in the "decolorizing" process. The steps are:

(1) Magnetic removal of iron impurities from the components to be used in the glass

(2) Oxidation of the remaining iron (generally in the form of FeO, which causes a bluish color) to ferric oxide (which produces a less objectionable tan color)

(3) Masking of remaining color by the addition of cobalt or selenium which complements the objectionable colors

The second step (oxidation) is where arsenic has been used and is still used to a limited extent.(62)

Special glasses having high infrared transmissibility sometimes contain arsenic as a component; such glasses are used in infrared cameras and in night-sighting reconnaissance systems. Infrared spectrometers used in such applications as nondestructive testing of plastics contain arsenic trisulfide.(39) Infrared lasers also use arsenic trisulfide in their glass components.(42)

Gallium arsenide has been used as window film and has also been considered for use in bulk form in windows for high-powered lasers; boron arsenide has found a possible application in the same area, but difficulty has been encountered in growing crystals of sufficient size. Combination of arsenic with tellurium, germanium, iodine, selenium, thallium, and sulfur has been used in specialty glasses having low melting-point properties.(42)

A note of interest is that the government ordered that arsenic not be used in fluorosilicate glass (of which Pyrex is the most well-known example) during World War II because the arsenic was needed elsewhere in the war effort. The producers of fluorosilicate glass didn't think it would be possible to comply, but they did, using the alternative oxidizers and fining agents discussed above.(62)

Electronics

Gallium arsenide was once considered as a potential replacement for silicon semiconductors, but silicon devices are currently favored because they are easier to fabricate and there is less hazard in materials handling. Arsenic is also used as a dopant for silicon materials, but only for certain special semiconductor properties; boron and phosphorus are the dopants of choice. Gallium arsenide semiconductors are preferred to silicon types in high-temperature conditions.(42)

Light Emitting Diodes (LEDs) rely heavily on arsenic intermetallic compounds. LEDs are used commonly in the latest generation of calculators; the diodes are arranged for digital readout, and their low power requirements make them ideal for battery-powered applications. Gallium arsenide, GaAs, and gallium arsenide phosphide, $GaAs_xP_y$, are the most commonly used, though indium arsenide and indium arsenide phosphide are used in some devices.(42)

Animal Dips

Sodium arsenite and potassium arsenite were the arsenicals used in dips for cattle. These compounds are now available only in laboratory-sized lots - no production quantities are available from American chemical manufacturers. There are no arsenical dips used any longer. Chemical suppliers and dip manufacturers have stopped production because of the risks and problems in the handling of inorganic arsenic.(64)

Arsenical dips have been replaced by formulations of Coumaphos or Toxaphene.(64)

Arsenic in Paint

Arsenic compounds have been used in paints both a pigments and as antifouling agents (marine uses). These uses, however, are in rapid decline - if, indeed, they exist at all any more.

According to the National Paint and Coatings Association - which represents 70 to 75 percent of the paint manufacturers and 90 to 95 percent of the paint sales - arsenic is no longer used in paint, either as a pigment or as an antifouling agent. The Marine Coatings Committee of NPCA says that arsenic is definitely not used as an antifouling agent in paints at this time.(65)

Note on Inorganic Arsenic Production

Many of the large suppliers of inorganic arsenicals - specifically potassium and sodium arsenite - have ceased this facet of their operations over the past several years. In telephone conversations with such chemical suppliers as Allied Chemical and Chipman Division (Rhodia), it was learned that EPA and OSHA rulings on registration and testing have made it unprofitable to handle arsenical compounds, especially since the demand for most inorganic arsenicals has been continuously decreasing over the past two decades.

Environmental Emissions Resulting from Arsenic Uses

Ferguson and Gavis estimate the average annual arsenic contribution by man to the environment (worldwide) is about 100,000 kkg/yr; this includes the amount which results from increased erosion processes resulting from excavation and mining operations. The total cultural contribution is believed to be on the order of 3 times the natural arsenic flow due to natural erosion processes. A significant portion of this - between 15 and 20 percent - results from the uses of arsenic.

Pesticides

Pesticides (insecticides, herbicides, and fungicides) are the largest single use of arsenic, and because pesticides are deliberately introduced into the environment, they account for about 80 to 90 percent of all arsenic emissions (onto land and into water and air) resulting from the uses of arsenic. In 1974, about 13,000 kkg of arsenic was consumed by pesticide manufacturers in the United States.(39) This is therefore the limiting amount of arsenic in pesticides that could reach the environment in 1974 (assuming no decrease in pesticide stockpiles for that year). Emissions not only result from the uses of pesticides, but from the manufacture of pesticides and from the disposal of such commodities as cotton gin trash and other agricultural wastes containing arsenical pesticide residues.

The EPA publication, Emission Factors for Trace Substances,(10) lists the emission factor for the production of pesticides as 10 kg As/kkg of arsenic processed. This emission results from handling losses of arsenic trioxide as it is transferred into reactor vessels. The 13,000 kkg of arsenic shipped to pesticide producers in 1974 corresponds to a total emission of 130 kkg.

Pesticidal emissions occur during the application of sprays and dusts, during the incineration of pesticide containers and agricultural waste, and as a result of evaporation processes. The emission factor given in the National Inventory of Sources and Emissions(9) is 168 kg As/kkg of arsenic applied as pesticide. (The remainder of the applied pesticidal arsenic is assumed to become firmly bound into the soil matrix.) Pesticidal emissions to the atmosphere resulting from the actual use of pesticides was on the order of 2184 kkg As in 1974.

Thus, in 1974, the latest year for which information is available, the total atmospheric emissions due to pesticide use was about 2300 kkg. The remainder of the 13,000 kkg used in pesticides in 1974 became either locked into insoluble solid systems (and is effectively removed from the environment) or found its way into natural water systems; there is no information available, however, upon which to base estimates of the portion of pesticidal arsenic which moves from the land into water systems; the range is probably on the order of 2 to 20 percent of the volume of pesticide used, i.e., between 260 and 2600 kkg.

Glass Manufacture

The EPA source(10) gives the emission factor for arsenic in glass production as 0.08 kg/kkg of glass produced; however, this is based on 1968 data, and since then the amount of arsenic used in glass production has decreased. The factor cited in the National Inventory is given in terms of the amount of arsenic used - 116 kg/kkg of arsenic used. The amount of arsenic used in glass in 1974 was 1805 kkg.(39) Thus, total atmospheric emissions in 1974 were on the order of 210 kkg. It is unlikely that arsenic in glass would find its way into the environment since it would be firmly fixed into the glass, except possibly as a consequence of recycling operations, but data on the amounts of arsenical glass recycled are not available.

Wood Preservatives

Atmospheric emissions resulting from the manufacture of wood preservatives is considered negligible. With regard to the uses of arsenically-preserved wood, however, it is reasonable to assume that after a sufficient period of time (decades and, in some applications, centuries) deterioration of the wood would release the arsenic to the environment. Such release would be very slow since the preservative compounds bind tightly to the wood fibers. The amount of arsenic moving into the environment by this method is too slow to pose a pollution hazard to air, water, or soil, and at the expected slow rate of release, concentration of soluble arsenic in adjacent soil and water would be low enough for the arsenic to become readily bound into insoluble species in soils and sediments.

Feed Additives

The pollution potential of arsenical feed additives is similar to that of pesticides in that arsenic is lost to the environment during both manufacture and as a result of use; the excreta of arsenically-fed animals is used as fertilizer, and since the arsenic in the feed additives passes through the animals in virtually the same amounts in which it is ingested, the arsenic eventually finds its way to the land where it undergoes the same processes which act upon the arsenical pesticides. However, whereas with pesticides a large portion of atmospheric emissions during application results from dusting, misdirected spray, volatilization, and so on, animal wastes are not subject to these mechanisms, and the arsenic contained in the excreta finds its way to the soil where it becomes bound into either insoluble soil complexes or, if in a soluble form, is carried into surface and ground water supplies. Animal excreta as a source of arsenic pollution is negligible, however, as has been shown in one study where no increase was found "in soil, water or forage after poultry litter containing from 15 to 20 ppm arsenic had been applied to land at a rate of 4 to 6 tons per acre per year for 20 years".(59)

With regard to the manufacture of feed additives, no emissions data are available. Using half the emission factor for the manufacture of pesticides — i.e., 5 kg As/kkg of arsenic used — the 409 kkg of arsenic used in feed additives in 1974 would have resulted in an atmospheric release of 2.04 kkg.

Nonferrous Alloying

The National Inventory of Sources and Emissions places the total atmospheric emissions of arsenic due to nonferrous alloying in 1968 at about 1/4 kkg. This is a negligible amount. In 1974 the amount of arsenic used in nonferrous alloying was on the order of three times the amount used in 1968, thus, the total emission would be on the order of 3/4 kkg, still a negligible amount.

A potential hazard might exist, however, in work environments where arsenical metals are melted or joined by fusion, as in the so-called "burning stations" in battery factories. Lead parts of batteries are fused together using a natural-gas flame for heating (a hand-performed process), and overheating could lead to the production of arsenic fumes. Specific data is not available.

Miscellaneous

The emissions factor for the miscellaneous uses of arsenic is given collectively as 2 kg/kkg of arsenic processed.(10) This factor is based on data for 1968, and different minor uses of arsenic prevail today. For example, arsenical animal dips and paint pigments and additives are no longer used, and the amount of inorganic arsenic used in such applications as leather tanning and non-feed-additive pharmaceuticals is on the decline - if still used at all. Electronics is probably the largest consumer of arsenic in the miscellaneous category, but emissions data for this use is lacking. Assuming that the major atmospheric emissions occur during handling and that the above emissions factor applies, then the 317 to 330 kkg of arsenic in miscellaneous uses in 1974 would result in an emission of about 0.65 kkg.

Non-Arsenical Alternatives

Pesticides

All pesticides are registered with EPA for use against specific pests in specific situations (e.g., with specific crops or industrial uses). EPA's Office of Pesticide Programs currently has a project underway to find alternatives to arsenical pesticides. The problem is a difficult one since the factors to be considered include cost of alternatives, method and cost of application, soil pH, regional climate, status of alternative (is it about to be banned or restricted?); availability of alternative, and possible side effects of alternatives on otherwise beneficial species.

An example of the magnitude of this problem of specifying alternatives is the case of lead arsenate as applied to apples. There are 15 apple pests which lead arsenate is registered to control. Of these, the number of registered alternatives varies from none (applethorn skeletonizer, case bearers, and others) to sixteen alternatives in the case of the codling moth. In addition to apples, ten other fruit crops are registered, along with associated pests and the registered alternative for each pest. Vegetables and non-crop uses must also be considered.

With regard to the vinyl fungicide 10,10'-OBPA, nonarsenical alternatives are available, but there is some question as to their relative effectiveness.

Wood Preservatives

The main alternatives to arsenical wood preservatives are creosote and pentachlorophenol. These alternatives, being oils, are not adequate substitutes in applications where aesthetics, discoloration, odor, or suitability for painting are important. This limitation dictated by the intended use is the major reason for the extensive use of arsenicals in lumber, timbers, and plywood; as opposed to the use of the preservative oils for poles, crossties, piling, etc. There are non-arsenical and non-oil-base alternatives: ACC (acid copper chromate) and CZC (chromated zinc chloride). However, CZC is not recommended for use where soil or water contact is encountered; and the health hazards from these alternatives may be equal to or worse than from the arsenical wood preservatives.

The Office of Pesticide Programs has also compiled a tentative list of registered alternatives to the arsenical fungicides used as "industrial wood preservatives". The list is tentative because (1) some of the substitutes are of limited availability or are only in limited use, (2) economic factors have not been taken into account, and (3) the alternatives might be more hazardous than the arsenicals.

Glass

Cerium oxide can be used in place of arsenic trioxide as a glass decolorizer and fining agent. Sulfates and nitrates may be used (and are being used) in place of arsenicals in fining, though for some glasses (as in tableware and TV tubes) the alternatives do not give as satisfactory a result.(42)

With respect to laser windows, alternatives are available, e.g., $Ge_{28}Sb_{12}Se_{60}$, $Ge_{28}Sb_{12}Te_{60}$, and the alkali halide materials (e.g., KCl) can replace $Ge_{33}As_{12}Se_{55}$. However, there are no alternatives for the unique properties afforded by arsenic trisulfide in certain glasses used as infrared lenses and windows.(42)

Feed Additives

Alternatives to feed additives used to improve weight gain and feed efficiency are hormones and antibiotics. Hormones, however, are restricted mainly to cattle because the withdrawal period prior to slaughter is too long to make the use of hormones profitable in poultry or swine.

Low level use of antibiotics in poultry feed will improve weight gain (2- to 3-percent improvement) and feed efficiency - though generally not to the same extent as will antibiotics in combination with arsenicals. Antibiotics will also prevent and control the same diseases prevented and controlled by arsenicals. The controversy and possible hazard of long-term use of antibiotic feed additives centers on the potential development of resistant strains of pathogens. It is possible for resistance factors to be transmitted between bacterial species; it is even considered possible that a nonpathogenic bacteria could pass a resistant gene to a pathogenic strain of the same bacterial type - the resultant pathogenic and resistant strain, if affecting man, would then not be amenable to treatment using the antibiotic to which the resistance had been developed. This problem is being studied by the FDA, and there is a movement to restrict the use of antibiotics in feed additives to those antibiotics which would not normally be used to treat diseases in people.(46,66)

Since hormones are not and cannot be economically used in poultry (the withdrawal period for hormones is too long to be of value in chickens — they go to market only 7 weeks after hatching), and since antibiotics have potential drawbacks, alternatives to arsenical feed additives are not readily available.

In discussing the disadvantages of arsenical feed additives with a feed-additive specialist at FDA,(46) the chief disadvantage cited was the 5-day withdrawal period required before slaughter - which required the producer to take the "positive action" of formulating a different feed mixture for those animals about to be slaughtered, as opposed to those animals for which slaughter is weeks away; arsenical feed additives are, for all practical purposes, not stored in muscle tissue.

An article in the British Medical Journal cites arsenical feed additives as an alternative to antibiotics in the control of piglet scour and turkey poult morbidity. Antibiotics are said to have "practical difficulties, apart from the risk of drug resistance". The use of arsenical feed additives is seen as an impetus to new studies of arsenic pharmacology. Arsenic in the livers of arsenically-fed pigs is supposedly so low that one would have to eat 110 lbs. of pork liver per day to consume a dangerous level of arsenic, though such a diet would present more than just a potential arsenic problem.(66)

Nonferrous Alloying

For most applications of arsenic in lead, copper, and brass, similar properties could be supplied by other materials, though increased cost would likely be a concern. In the case of lead-acid batteries, an industry spokesman stated that there are no known alternatives to arsenical lead in batteries at this time.(61)

Electronics

Light Emitting Diodes (LEDs) are based on gallium arsenide compounds for which there are no alternatives. However, LEDs themselves could be replaced by gas-discharge displays, incandenscent bulbs, and (soon to be available) liquid crystal displays - none of which will supply the complete complement of advantages of LEDs such as ruggedness, low power requirement, high visibility, and compatability with semiconductor circuitry.(42)

Other arsenical semiconductor uses are based upon the specific electrical and chemical properties of arsenic, and to the extent that these properties can be compromised, alternatives are available.(42)

SECTION V

INDUSTRIAL SOURCES OF ARSENIC MOBILIZATION

The natural occurrence of arsenic in the earth's crust is 2 to 5 ppm, but higher-than-average concentrations occur in metallic ores of two types: in sulfide deposits (associated with copper, lead, zinc, and other ores); and in sedimentary deposits such as iron ore, phosphate rock, borax ore, manganese ore, and fossil fuels.

The very high temperatures associated with smelting of metallic ores generally result in the release of a large portion of the naturally-occurring arsenic to the atmosphere. Both elemental arsenic and its common oxide, As_2O_3, are extremely volatile materials at common smelting temperatures: arsenic sublimes at 613°C; As_2O_3 sublimes appreciably at 135°C and fully at 315°C.

Three other factors, aside from the inherent volatility of As_2O_3, contribute to the generally high losses of this material to the atmosphere:

1. The As_2O_3 is slow to condense as higher-temperature flue gases are cooled; a very long time is required for nucleation and growth of the particles. This phenomenon is the reason why the commercial process for As_2O_3 manufacture includes several high-volume condensation chambers (called kitchens) arranged in series at successively lower temperatures from 220°C in the first to 100°C or less in the last.(2,22,24,37,38) The same technology is used in the commercial manufacture of P_2O_5, only the "kitchens" are called "barns".(77) Hence, As_2O_3 may very well pass through baghouses and electrostatic precipitators as a supersaturated vapor even if the temperature is below the equilibrium sublimation temperature.
2. Dust collection devices such as electrostatic precipitators and baghouses are routinely operated at elevated temperatures so as to stay well above the dew point of the flue gas. For many metallurgical operations such as roasting and sintering,

the flue gases have a very high moisture content, necessitating high dust collection temperatures.

3. It is common practice in the nonferrous metals industry to recycle collected flue dusts to the process until concentrations of valuable metals build up to an economically-processable level. At each stage of recycle, the very volatile As_2O_3 has another opportunity to escape collection.

Each segment of the nonferrous metals industry will be examined to determine the quantities of arsenic involved in the industry and the fate of this arsenic. The quantities of arsenic in commercially-developed sedimentary deposits will also be investigated.

The Primary Zinc Industry

Table 2 lists the arsenic content of representative zinc concentrates (comparable data for domestic concentrates were not available). The average ratio of arsenic to zinc in these concentrates is about 1,050 ppm.

The quantity of zinc produced from concentrates in the U.S. for the past several years is listed in Table 3. The domestic slab zinc production has been decreasing in a rather dramatic fashion, primarily because foreign consumption of zinc has grown rapidly. Since the U.S. always had to import ore concentrates the domestic competitive position deteriorated as its share of demand decreased and as foreign metal production capacity increased. Other major factors contributed to the decline in U.S. zinc production. Older pyrometallurgical plants, especially horizontal retort plants, are closing because they are labor-intensive, because they have severe air pollution problems, and because they cannot manufacture the high grades of zinc. Only two small U.S. horizontal retort plants are still in operation, and account for only 13 percent of the total U.S. production capacity of 689,000 kkg/year. The two large pyrometallurgical plants (one vertical retort plant and one electrothermal plant) account for 48 percent of the U.S. capacity, and the three electrolytic plants account for the remaining 39 percent.

Table 2

Arsenic Content of Zinc Concentrates

Source of Concentrate	Arsenic Content, ppm	Zinc Content, Percent	As/Zn, ppm	Reference
Broken Hill, Australia	500	51.0	980	67c
Broken Hill, Australia	700	53.7	1,300	67c
Broken Hill, Australia	1,170	52.1	2,240	67c
Broken Hill, Australia	610	52.9	1,150	67c
Valleyfield, Quebec	350	52.9	660	67b
Cartagena, Spain	200	49.3	410	67a
Cerro de Pasca, Peru	640	59.2	1,080	74a
Mt. Isa, Australia	350	50.4	700	74a

Table 3

Primary Zinc Refined in the U.S., Metric Tons/Year

Sources: Bureau of Mines (18, 70)

Year	From Domestic Concentrates	From Imported Concentrates	Total
1968	452,000	473,000	925,000
1969	416,000	527,000	943,000
1970	366,000	429,000	795,000
1971	366,000	329,000	695,000
1972	363,000	211,000	574,000
1973	311,000	180,000	491,000
1974	281,000	209,000	490,000

Two new electrolytic plants are either planned or being constructed, and the two remaining horizontal retort plants are being phased out. It appears that the decline in domestic zinc production has been halted and possibly reversed. For the purposes of this study, the 1973-74 production level of 490,000 kkg/year will be used, with 290,000 kkg/year pyrometallurgical and 200,000 kkg/year electrolytic. Based upon this level, the zinc concentrates processed annually in the U.S. contain 520 kkg of arsenic. Refined zinc of all commercial grades, and commercial zinc oxide (either French or American process), contain no appreciable (greater than 10 ppm) arsenic,(15,67d,e) equivalent to less than 5 metric tons per year.

In the primary zinc process, the arsenic in the zinc concentrate is largely retained through the roasting process, as indicated by data from both a multiple-hearth furnace and a fluid-bed furnace.(67a) In pyrometallurgical zinc smelters, all of the arsenic remaining in the calcine (from the roaster) is volatilized in the sintering operation, with large losses to the atmosphere. At one sintering plant, the dusts collected in a baghouse contain 15.0 percent As_2O_3.(67d) These dusts are then processed for cadmium recovery; one route involving burning of the dusts which volatilizes more of the arsenic. Other routes to cadmium recovery from flue dusts involve oxidative leaching, in which ferrous sulfate is added to precipitate the arsenic as ferric arsenate. This residue, normally disposed of on land, amounts to 1.8 kg per metric ton of pyrometallurgical zinc produced, or 520 kkg/year.(75)

Davis reported on air emission factor from pyrometallurgical zinc smelters of 0.65 kg of arsenic per kkg of zinc produced.(9) Based upon a pyrometallurgical zinc production level of 290,000 kkg/year, the arsenic air emissions amount to 190 kkg/year. Since the zinc concentrates processed pyrometallurgically originally contained 310 kkg/year of arsenic, the difference of 120 kkg/year may be assumed to be in the residues sent to disposal. Although other solid wastes from the primary zinc industry amount to 1.50 kkg per kkg of zinc produced,(75) there should be no appreciable arsenic in either the acid plant sludge (which arises from the roasting operation, upstream of where the arsenic is volatilized) or in residues from retorting and ZnO production (downstream of where the arsenic is volatilized).

In electrolytic zinc refineries, the arsenic in the calcine (the roasted zinc concentrate) ends up in the residue from the acid leaching operation (which dissolves the zinc). This residue amounts to 360 kg per metric ton of zinc produced; it contains significant quantities of lead, copper and cadmium and is shipped to a lead smelter.(68,69a,75) This residue, amounting to 72,000 kkg/year (dry basis), contains virtually all of the 210 kkg/year of arsenic originally in the zinc concentrates which are refined electrolytically, plus 8,100 kkg/year of lead (based upon a ratio of lead to zinc of 0.0165 in zinc concentrates).

The arsenic found in wastewaters from primary zinc refining are summarized in Table 4. The resulting recommended effluent limations(69a) (30-day averages) were 8.0×10^{-4} kg of arsenic per metric ton of zinc produced (1977) and 5.4×10^{-4} kg of arsenic per metric ton of zinc produced (1983). These values are equivalent to 0.4 kkg/year (1977) and 0.3 kkg/year (1983) of arsenic in wastewater effluents. No special control and treatment is required for arsenic, over and above standard water use minimization and segregation and lime-and-settle treatments; and no control and treatment costs are directly attributable to arsenic removal.

In summary, the distribution of the arsenic originally in the zinc concentrates is as follows:

Loss to atmosphere,	190 kkg/year
Retained in zinc products,	5 kkg/year
In land-destined wastes,	120 kkg/year
In wastewater effluents,	0.4 kkg/year
In residues shipped to lead smelters,	210 kkg/year
Total	525 kkg/year

The Primary Lead Industry

As Table 5 indicates, the arsenic content of representative lead concentrates varies from about 600 ppm to 1,500 ppm (comparable data for domestic

Table 4

Arsenic in Wastewaters from Zinc Smelting

Source: EPA

Plant	Contributing Operations	Arsenic, kg/kkg Zinc
B	Roasting and Electrolysis	<0.0001
D	Roasting, Leaching, Electrolysis, Casting	0.01
F	Pyrolytic Smelting	0.0002
H	Horizontal Retort	0.000004
B	Acid Plant	0.003
B	Metal Casting Cooling	<0.00008
B	Auxiliary Metal Reclamation	0.000017
B	Auxiliary Metal Reclamation	0.011

Table 5

Arsenic Content of Lead Concentrates

Source of Concentrate	Arsenic Content, ppm	Lead Content, Percent	As/Pb, ppm	Reference
Broken Hill, Australia	1,530	70.1	2,180	67c
Broken Hill, Australia	1,200	74.0	1,620	67c
Broken Hill, Australia	1,111	75.9	1,470	67c
Broken Hill, Australia	570	75.8	750	67c
Cerro de Pasca, Peru	600	43.7	1,370	74b
Casapalca, Peru	800	61.7	1,300	74b
Boliden, Sweden	800	74.9	1,070	74c

concentrates were not available). The average ratio of arsenic to lead in these concentrates approximately 1,400 ppm, will be used to estimate the overall quantities of arsenic contained in lead concentrates.

Table 6 lists the quantity of lead produced from concentrates in the United States for the past several years. The primary lead produced since 1970 has been relatively stable at about 610,000 kkg/year, implying that the quantity of arsenic in these concentrates is 850 metric tons per year. An additional 210 metric tons of arsenic per year enters the primary lead industry via residues from the electrolytic zinc industry, so that the estimated total quantity of arsenic entering the lead industry is 1,060 metric tons per year.

The refined lead product has specifications (ASTM B29-55) which limit the total of arsenic, antimony, and tin to 20 ppm for undesilverized lead; and to 50 ppm for desilverized lead. Hence, the final refined lead contains no more than about 20 kkg/year of arsenic. Hence, virtually all of the arsenic is removed in the smelting and refining process, in one or more of the following forms:

1. A constituent in slags or sludges (as an arsenate)
2. A constituent in collected dusts and fumes (as As_2O_3)
3. An air emission pollutant (as As_2O_3)

In the smelting of lead concentrates, some arsenic is volatilized in a sintering operation, and some is removed via the slag from the lead blast furnace; but much of the arsenic remains with the lead in the base bullion product from the blast furnace.(68)

The base bullion passes through a drossing operation for copper removal. A subsequent oxidation process with a fluxing agent (called a "softening" operation) removes the arsenic as well as antimony, tin, and residual copper from the bullion as a calcium or sodium arsenate in a slag layer. The blast furnace and lead refinery slags are sent to a zinc fuming furnace, but the stable arsenates remain with the slag. Small quantities of arsenic remaining in the softened lead are removed either via fire-refining (as a fume or a slag) or via electrolytic refining (as a sludge).

Table 6

Primary Lead Refined in the U.S., Metric Tons/Year

Sources: Bureau of Mines (18,70)

Year	From Domestic Concentrates	From Imported Concentrates	Total
1968	316,000	107,000	423,000
1969	465,000	113,000	578,000
1970	479,000	126,000	605,000
1971	519,000	70,000	589,000
1972	537,000	93,000	630,000
1973	532,000	92,000	624,000
1974	526,000	82,000	608,000

Davis(9) and Anderson(10), based upon material balance data, reported on emission factor for lead smelters of 0.4 kg per metric ton of lead. Based upon an annual lead production of 610,000 metric tons, the arsenic lost to the atmosphere is 240 kkg/year.

Arsenic was not found in any appreciable quantity in the wastewaters from primary lead smelters; the slag granulation operation has a closed water loop, and sludges from wet scrubbers are lime-treated (precipitating the arsenic) and settled prior to discharge.(69b,75)

The solid wastes per metric ton of lead product amount to 410 kg of slag plus 40 kg of settled sludges (dry basis).(75) Based upon a production level of 610,000 kkg/yr; the solid wastes amount to 274,000 kkg/year. The remainder of the arsenic entering the lead industry, less the losses to the air and the quantity retained in lead products, amounts to 800 metric tons per year and reports in the solid wastes from the lead industry. An average concentration of arsenic in these wastes of 0.29 percent is implied from this analysis; it compares favorably with two separate values, both 0.2 percent, for the arsenic content of lead blast furnace slag.(74b,c)

In summary, the distribution of the arsenic originally in the lead concentrates (850 kkg/year) and in residues from the zinc industry (210 kkg/year) is as follows:

Loss to atmosphere,	240 kkg/year
Retained in refined lead,	20 kkg/year
In land-destined wastes,	800 kkg/year
Total	1,060 kkg/year

The Primary Copper Industry

Table 7 lists the quantities of domestic copper ore, and the copper in ore concentrates processed in the United States during the past several years; the primary domestic copper production has averaged about 1.60 million metric tons per year. Of interest is the average copper content of ores; first, the concentration is low compared to most other metallic minerals; and second, the concentration is decreasing with time (i.e., poorer ores are being mined as time

Table 7

Primary Copper in the U.S.

Sources: Bureau of Mines (18,70)

Year	Domestic Ores Mined		Copper from Ore Concentrates, kkg/yr		
	Ore, kkg/yr	% Cu in Ore	From Domestic Concentrates	From Foreign Concentrates	Total
1968	154,200,000	0.60	1,054,000	251,000	1,305,000
1969	202,900,000	0.60	1,331,000	248,000	1,579,000
1970	233,800,000	0.59	1,380,000	221,000	1,601,000
1971	220,100,000	0.55	1,280,000	164,000	1,444,000
1972	242,000,000	0.55	1,524,000	175,000	1,699,000
1973	263,100,000	0.53	1,559,000	135,000	1,694,000
1974	-	-	1,440,000	30,000	1,470,000

progresses). This latter trend has been continuing for quite some time; ores mined in 1900 averaged 4 percent copper. The first U.S. porphyry ores mined in the 1905-1915 period had 2 percent copper. The average copper content of domestic ores in 1950 was 1 percent, and it is projected that the grade will decline to 0.25 percent by the year 2,000.(78)

The arsenic content of copper ores and concentrates is highly variable. Ores from New Mexico and Arizona have much lower arsenic concentrations than ores from Montana. Data is extremely sparse, especially in recent years. A circa 1913 copper ore from Butte, Montana, contained 3.25 percent copper and 0.37 percent arsenic (a ratio of As/Cu of 0.114).(21) More recently, Butte ores have contained 0.6 percent copper and 0.1 percent arsenic (As/Cu = 0.17);(30,79) and Butte ore concentrates have contained 26 percent copper(79) and 1.6 percent arsenic(20) for a ratio of As/Cu = 0.062. In 1963, a Colorado copper ore had a ratio of As/Cu of 0.0028.(2) Also, in 1963, a copper concentrate from Highland Valley, British Columbia, assayed 41.54 percent copper and 0.012 percent arsenic (As/Cu = 0.0029).(80) In northern Chile, copper ore assayed 0.054 percent arsenic, and the copper concentrate contained 1.64 percent arsenic (As/Cu $\simeq$ 0.06).(2)

The U.S. Bureau of Mines bases its estimate of domestic arsenic reserves, 1.72 million metric tons, upon its estimate of domestic copper reserves, 77.6 million metric tons.(17) An inferred ratio of arsenic to copper in copper ores and concentrates is therefore 0.022. While the data for specific ores, quoted in the previous paragraph, have As/Cu ratios highly divergent from 0.022, this value will be used for the purposes of this study. Based upon a primary copper production level of 1.60 million metric tons per year, it is estimated that 35,000 metric tons per year of arsenic accompany the copper concentrates to the smelters.

Refined copper is manufactured to very stringent purity specifications, since small quantities of impurities adversely affect its electrical and mechanical properties. Electrolytic copper has a specification (ASTM B224) for 0.01 percent maximum impurities other than oxygen; the specifications for deoxidized copper and oxygen-free copper are equally demanding. Normally, electrolytically-refined copper contains arsenic at levels reported as 1 to 10 ppm,(81) and 4 to 11 ppm.(82)

Of the total copper production of 1.60 million kkg/year, approximately 1.46 million kkg/year is electrolytic;(70) at an average arsenic concentration of 5 ppm, the quantity of arsenic in the product copper is about 7 kkg/year. Another 80,000 kkg/year is fire-refined casting copper,(70) with a specification of 75 ppm maximum arsenic content,(20) implying a maximum quantity of 6 kkg/year of arsenic. The remaining 60,000 kkg/year of copper is lake (elemental) copper,(70) not derived from concentrates. There are three grades of lake copper: Prime, which contains 25 ppm arsenic; Natural, which contains 200 to 600 ppm arsenic; and Arsenical, with 600 to 5,000 ppm arsenic (primarily used in making arsenical copper alloys).(83) At an average of 500 ppm, the total quantity of arsenic in lake copper would be 30 kkg/year.

Of the total arsenic in copper concentrates, 35,000 kkg/yr, only about 13 kkg/yr remains in the refined copper, the remainder being removed in the smelting and refining operations upon copper concentrates (which contain between 15 and 35 percent copper). Roasting of copper concentrates is an optional first step. Older plants built in the 1930's incorporated roasting since ore concentrators at that time were unable to reach a sufficiently low level of iron sulfide; recent advances in separation technology have made the overall sulfur content of the concentrate low enough to bypass the roasting operation. An additional important factor is the arsenic and antimony content of the concentrate; roasting is often required for their partial removal prior to smelting.(68,69c,75,84)

Roasting is either accomplished in the older multiple-hearth units or in fluidized beds, at temperatures approaching 1,000°C.(68) A significant portion of the arsenic is driven off; in a 1913 Anaconda roaster flue gas where the SO_2 (plus SO_3) concentration was 2.82 percent, the As_2O_3 concentration was 0.0073 percent.(87)

Either roasted or unroasted concentrates are smelted in reverberatory furnaces or blast furnaces at 1,100 to 1,650°C.(68,84) The products are matte (a copper and iron sulfide material, containing approximately 30 percent copper), slag (oxides of iron, silicon, calcium, and aluminum), and SO_2-bearing flue gas. Of the total sulfur content of the concentrate (nominally 31.5 percent S and 27.5 percent Cu), up to 20 percent is liberated during smelting in a reverberatory furnace.(84) The 1913 Anaconda data for the reverberatory flue gas was 0.427 percent SO_2 (plus SO_3) and 0.0156 percent As_2O_3.(87) In one copper blast furnace operation, the dusts collected by a cyclone and then by a baghouse (downstream of the cyclone) are:

	Percent of Total Charge	Cu Content, Percent	As Content, Percent
Cyclone Dusts	1.75	26.35	1.09
Baghouse Dusts	1.26	1.35	7.77

These data strongly indicate that much of the arsenic is vaporized during smelting.

The next step is converting the matte to blister copper by blowing with air or oxygen in the presence of a silica flux. The iron is converted to an iron silicate slag, the remaining sulfur is oxidized to SO_2, and volatile impurities such as arsenic and lead are largely released. Then, the blister copper is fire-refined to "anode" copper by further blowing with air; more SO_2 is driven off, and more iron, zinc, and tin are removed via a silicate slag. Finally, the anode copper is electrolytically refined, removing almost all of the residual impurities.

Table 8 lists representative arsenic levels in the copper as it progresses in refining from the concentrate (which nominally has a ratio of As/Cu of 22,000 ppm), to copper matte, to blister copper, to anode copper, and finally to the cathode copper product (which nominally has a ratio of As/Cu of 5 ppm). These data show that the roasting and smelting operations remove approximately 70 percent of the arsenic from the copper, reducing the arsenic content from 22,000 ppm (2.2 percent) to 6,400 ppm (0.64 percent). The data of Table 8 indicate that the arsenic contents of blister copper and anode copper are approximately the same; if a value of 900 ppm (0.09 percent) is taken, then 25 percent of the arsenic originally in the copper concentrate is removed in the converter. The remaining 5 percent of the original arsenic is virtually all removed by electrolytic refining.

Slag from smelting in reverberatory furnaces amounts to 3 metric tons per metric ton of copper produced.(75) A copper blast furnace slag assayed about

Table 8

Arsenic Content of Copper in Various Stages of Refining

Copper Matte		Blister Copper		Anode Copper	
Ref.	As/Cu, ppm	Ref.	As/Cu, ppm	Ref.	As/Cu, ppm
74d	6,600	68,69c	200	82,86	200
74d	6,900	68,69c	1,000	82,86	100
74d	6,800	68,69c	350	82,86	40
74d	6,100	76	10	82,86	60
74d	6,700	76	370	82,86	1,500
82	5,400	76	70	82,86	1,600
		82	80	82,86	3,200
		82,86	2,300	82,86	1,900
		82,86	100	82,86	500
		82,86	100	82,86	1,000
		82,86	200		
		82,86	1,000		
		82,86	1,500		
		82,86	4,000		
Avg.	6,400	Avg.	800	Avg.	1,000

0.04 percent arsenic, which amounted to 5 percent of the arsenic originally in the concentrate;(74d) assuming there were 0.022 kkg of arsenic per kkg of copper in the concentrate, a slag quantity of 2.75 kkg per kkg copper produced is implied. At another plant, 2.56 kkg of reverberatory slag plus 1.77 kkg of converter slag are produced per metric ton of copper product.(88) Hence, for each metric ton of copper produced, about 3 metric tons of slag are produced which contain 1.2 kilograms of arsenic.

Of the 0.9 kg of arsenic per metric ton of copper product which remain in the anode copper, 0.22 kg are found in the slimes from the electrolysis cells, and 0.68 kg are found in the electrolyte.(82) The slimes are filtered and the electrolyte bleed is evaporated yielding a sludge; both streams together amount to 3.0 kg (dry basis) per kkg of copper product(75) and contain the 0.9 kg of arsenic, implying an arsenic concentration of 30 percent. These wastes are further processed for precious metals recovery, and the arsenic eventually is disposed of on land as a slag resulting from smelting with a basic flux.(68)

The raw wastewaters from the primary copper industry are from four main sources, and the quantities of arsenic are as follows:(69c)

Slag Granulation Water,	0.19 kg As/kkg Cu Product
Acid Plant Blowdown,	0.06
Contact Cooling Water,	0.00
Electrolytic Refining,	0.03
Total	0.28 kg As/kkg Cu Product

Control and treatment technology emphasizes recycle and reuse of these acidic wastewaters, plus lime treatment (with ferric chloride flocculant) and sedimentation. One new treatment facility will reduce the arsenic concentration of the wastewaters from 9.4 mg/l to 1.2 mg/l; an existing facility shows no reduction from about 10 mg/l, while a third shows a reduction from 0.85 mg/l to 0.73 mg/l.(69c) The recommended 1977 effluent limitation guidelines (30-day averages) are based upon a concentration of 10 mg/l arsenic in the effluent, equivalent to 0.02 kg of arsenic per metric ton of copper product. Based upon a 90 percent reduction in the quantity of wastewater, the recommended 1983 effluent limitations guideline calls for 0.002 kg of arsenic per metric ton of product copper. The estimated costs for compliance (not all attributable to arsenic control and treatment, of course) are:

	1977	1983
Capital Costs	$334,000	$1,581,000
Annual Operating Costs	$118,000	$ 805,000

Thus far, of the original 22 kg of arsenic per metric ton of copper, only 2.4 kg have been accounted for: 1.2 kg in slag, 0.9 kg in slimes and sludges, and 0.3 kg in raw wastewaters. Hence, almost 20 kg of arsenic per kkg of copper are in the flue gases from roasting and smelting and from converting. Since 70 percent of the original arsenic, or 15.4 kg/kkg, is lost in roasting and smelting, and since 1.2 kg/kkg reports in the slag, the quantity of arsenic in the roasting and smelting flue gases amounts to 14.2 kg/kkg. Similarly, the 25 percent of the original arsenic lost in converting, 5.5 kg/kkg, must be in the converter flue gases.

It is important to note that the predominant loss of sulfur is opposite to the loss of arsenic. The S/Cu ratio is about 1.15 in the concentrate, about 0.80 in matte (after roasting and smelting), and about 0.15 in blister (after converting).(68) While two-thirds of the arsenic is lost in roasting and smelting, only one-third of the sulfur is lost in these steps. In the past, it was general practice for byproduct sulfuric acid to be made from converter gases, while roasting and reverberatory gases are released to the atmosphere after particulate control.(69c) The SO_2 concentration in roasting and reverberatory gases is generally too low for economical SO_2 recovery. Recent air pollution regulations calling for an overall 90 percent recovery of sulfur oxides would require an additional capital investment by the copper industry estimated to be in excess of $250 million.(79,84,89,90,91,92) The impact of additional sulfur oxides control has been to force process changes whereby roasting and smelting gases as well as converter gases, are used for acid manufacture.

Since converter flue gases are predominantly used for acid-making, the 5.5 kkg of arsenic in these gases should appear in the acid wasted from cold-gas cleaning of the SO_2 prior to catalytic conversion to SO_3. Hot gas cyclones and hot electrostatic precipitators upstream of the cold-gas cleaning operation should not remove appreciable As_2O_3 because of its reluctance to condense. The cold-gas venturi scrubbers and packed towers, however, should be extremely effective in removing the acid-soluble As_2O_3.(91) The commercial sulfuric acid byproduct from copper smelters contains no more than 0.5 ppm arsenic, verifying the effective removal of arsenic.(158) The arsenic-containing scrubber liquor may be treated for removal of the arsenic (and other contaminants) with subsequent land disposal, or it may be used as a waste acid in the copper mining operation as a leach liquor. This latter route is thought to be more common; in this case, the arsenic is eventually bound to the ore residues (as ferric arsenate). For the purpose of this analysis, this 8,800 kkg/year of arsenic will be thought of as arsenic dissipated to land.

The flue gases from roasting and smelting are generally passed through cyclones, "balloon flues", electrostatic precipitators, and baghouses, for particulate control. As was discussed previously, these techniques have limited success in capturing As_2O_3. At one copper blast furnace, the dust collection system consisted of bag filters downstream of cyclones. The cyclones captured 8 percent of the arsenic in the flue gas, the bags captured 41 percent, while 51 percent escaped collection.(74d)

The emission factor reported by Davis(9) and by Anderson(10) is 3 kg of arsenic per metric ton of copper product. Since the arsenic in the roasting and smelting flue gases amounts to 14.2 kg per kkg, it is implied that 11.2 kg per kkg are collected and that the collection efficiency is 79 percent.

These collected dusts are the source of commercial white arsenic in the United States, produced solely be ASARCO at Tacoma, Washington. If all the dusts collected at all of the copper smelters were shipped to ASARCO/Tacoma, the 11.2 kg of arsenic per metric ton of copper product multiplied by a copper production level of 1.60 million metric tons per year would be equivalent to 17,900 metric tons per year of arsenic or to 23,600 metric tons per year of As_2O_3. However, the ASARCO production level of white arsenic has been reported to be about 7,300 kkg/yr according to one source(42) and about 33 kkg/day (or 11,000 kkg As_2O_3/yr) according to another source.(69c) The plant capacity for producing white arsenic at Tacoma is on the order of 11,000 kkg/year.(42) The difference between the estimated flue dusts collected and the commercially-produced white arsenic is 12,600 kkg/year of As_2O_3, or 9,600 kkg/year of elemental arsenic, or 6.0 kg As/kkg of copper produced. An explanation is that not all flue dusts collected at copper smelters are shipped to ASARCO; this is verified by the EPA estimate that within the copper industry flue dusts are deposited on land at a rate of 17 kg flue dust per metric ton of copper produced.(75) An ASARCO spokesman(39) has stated that in 1974 the amount of white arsenic shipped from the Tacoma plant was about 16,400 kkg. Since the capacity of the Tacoma plant is 11,000 kkg As_2O_3/year, the excess 5,400 kkg must have come from ASARCO stockpiles.

In summary, the distribution of the arsenic originally in the copper concentrates (or native copper) is as follows:

In lake copper product	30 kkg/year
In fire-refined copper product	6 kkg/year
In electrolytic copper product	7 kkg/year
In slags to land disposal	1,900 kkg/year
In sludges to land disposal	1,500 kkg/year
In flue dusts to land disposal	9,600 kkg/year
In leach residues dissipated to land	8,800 kkg/year
In treated wastewaters	32 kkg/year
In air emissions	4,800 kkg/year
In commercial white arsenic	8,300 kkg/year
Total	35,000 kkg/year

Other Primary Nonferrous Metals

Arsenic, at concentrations significantly greater than the average crustal concentration of 2 to 5 ppm, occurs in sulfide ores of nonferrous metals other than zinc, lead, and copper. Among these are ores of gold, silver, mercury, uranium, vanadium, and antimony. Table 9 lists the U.S. production levels of these metal ores.

Very little data is available on the arsenic content of these ores, or on the fate of the arsenic during the mining, milling, smelting, and refining operations. Arsenic occurs at 3 percent of antimony in antimony ores; it is recovered (and sold) via a sulfide precipitation step in the hydrometallurgical Sb_2O_3 process. Arsenic did show up at appreciable concentrations in the raw waterborne wastes from mining and milling operations:(75)

Source	Arsenic Concentration in Raw Waste, mg/l
Gold Mines	0.03 - 0.08
Gold Mills	0.05 - 3.5
Silver Mills	0.07 - 3.5
Mercury Mills	0.02 - 0.38
Uranium Mines	0.01 - 0.03
Uranium Mills	0.1 - 1.5
Vanadium Mills	0.35
Antimony Mills	0.23

For the purposes of this study, a very rough estimate of the quantity and fate of arsenic is based in part upon the similarity of these minor nonferrous metal ores and recovery processes to the lead-zinc industry, and in part to the data for antimony. It is assumed that the arsenic in ore concentrates is one percent of the quantity of each of the metals in Table 9; and that one-third is recovered as sulfides and sold as pigments, that one-third is lost to the atmosphere and that one-third is in land-destined wastes.

Based upon a total production level of 15,000 metric tons per year for all of the metals in Table 9, the arsenic involved is 150 metric tons per year, of which 50 kkg/year is recovered for commercial purposes.

Arsenic in Nonferrous Metal Products

The quantity of metallic arsenic used in 1974 for non-ferrous alloying is between 540(18,70) and 1,240(39) metric tons. In addition, it was previously estimated that the quantities of new arsenic retained in refined primary metals are:

Table 9

Other Primary Non-Ferrous Metal Ores Mined in the U.S.

Metric Tons/Year of Metal Content

Sources: Bureau of Mines[18,70]

	1970	1971	1972	1973	1974
Gold	54.1	46.6	45.1	36.7	34.9
Silver	1,400	1,295	1,155	1,175	1,050
Mercury	941	616	253	75	59
Uranium	9,360	9,430	9,900	9,920	8,910
Vanadium	4,830	4,760	4,420	3,970	—
Antimony	1,025	930	443	494	544

In Zinc,	5 kkg/year
In Lead,	20 kkg/year
In Lake Copper,	30 kkg/year
In Fire-Refined Copper,	6 kkg/year
In Electrolytic Copper,	7 kkg/year
Total,	68 kkg/year

Arsenic at one percent concentration(42) in lead shot amounts to 60 metric tons per year.(47) This arsenic, used to enhance the sphericity of the lead shot, should be all new arsenic since no lead shot is recycled.

Arsenic is also used at about 0.6 percent in lead-tin bearing metals (babbitts).(42,60) In 1971 and 1972, the quantity of lead consumed for bearing metals was 14,600 metric tons per year;(70) since the lead content of babbitt metal is 83 percent, the arsenic quantity is approximately 175 metric tons per year. However, babbitt metal is extensively recycled, with 12,500 kkg of lead recovered in 1972 from babbitt metal scrap.(70) By difference, only 2,100 kkg/year of new lead is consumed in bearing metals. Since the melting point of lead (326°C) and of babbitt metals (260-270°C) is low compared to the vaporization temperature of arsenic (613°C), little arsenic is lost in secondary lead kettle refining. Hence, about 150 kkg/year of the arsenic is recycled, while 25 kkg/year is new arsenic.

Antimonial lead (hard lead) is used primarily for the posts and grids of lead-acid storage batteries, and for lead cable sheathing.(60) The arsenic concentration of such alloys ranges from 0.15 percent for arsenical lead, to no more than 0.5 percent for antimonial lead.(42,60) An arsenic content of 0.25 percent will be used for the purposes of this study. In the 1971-1972 time period, the lead consumption for these purposes was:(70)

Battery posts and grids	303,000 kkg/year containing 760 kkg As/yr
Cable covering	45,000 kkg/year containing 110 kkg As/yr
Total	348,000 kkg/year containing 870 kkg As/yr

It is therefore inferred that 870 metric tons per year of arsenic is contained in lead alloys for batteries and for cable covering.

Like babbitt metals, antimonial lead is extensively recycled. In 1972, 322,000 metric tons of lead was recovered from old antimonial lead scrap and old cable convering scrap,(70) which must have contained 805 kkg of arsenic (at 0.25 percent). Conversely, only 6,800 metric tons of primary antimonial lead was manufactured in 1972.(4) Antimonial lead is recovered in lead blast furnaces,(121), and much of the arsenic accompanies the lead through this process.(2) Using the air emission factor for lead smelters, 0.4 kg of arsenic per metric ton of lead;(9,10) the concentration of arsenic in lead blast furnace slag, 0.2 percent;(74b,74c) and the quantity of slag from secondary lead blast furnaces, 148,300 kkg/year;(75) the 805 kg/year of arsenic is distributed as follows:

Loss to atmosphere	130 kkg/year
In slag to land disposal	300 kkg/year
Retained in secondary lead (by difference)	375 kkg/year

The difference, then, between the 870 kkg/year of arsenic in lead alloys produced, and the 375 kkg/year of arsenic retained in recycled lead, is 495 kkg/year of new arsenic which must be added.

Arsenic, at a concentration of 0.03 percent, is used in Admiralty brass for condenser and heat-exchanger tubing.(42,60,81) This alloy contains 71 percent copper. In 1968, the copper demand for all industrial non-electrical machinery was 250,000 metric tons;(17) if 10 percent of this is taken as an extreme estimate of the Admiralty brass production, the quantity of arsenic involved would be 7.5 metric tons per year. A much more important use for arsenic-containing copper is for automotive radiators, where a nominal 0.3 percent of arsenic is used. A typical auto radiator weighing 6.6 kilograms contains 5.9 kilograms of copper;(120) at a production level of 10 million autos (and other vehicles) per year, 59,000 kkg/year of copper containing 175 kkg/year of arsenic are consumed. Because of the high value for scrap copper, virtually all auto radiators are recycled. In 1972, the consumption of old unsweated auto radiators amounted to 67,000 metric tons.(70)

Auto radiator scrap is therefore the predominant form of arsenic-bearing scrap copper. This category of scrap is normally not processed in blast or cupola melting furnaces (which are used for lower-grade scrap, slags, and drosses), but is fire-refined.(122) It was earlier shown in the discussion of the primary copper industry that fire-refining removes little if any arsenic from elemental copper; this is substantiated upon theoretical grounds which show that arsenic in elemental copper is most difficult to either oxidize or volatilize.(85) Hence, it may be concluded that the arsenic in secondary copper remains with the product. Some of this secondary refined product is later electrolytically refined (removing arsenic and other impurities), and some is directly used. Scrap segregation practices are common in the secondary copper industry(121,122) to meet product purity requirements by careful blending of available scrap; it appears that some of the arsenical copper scrap would be used in manufacturing arsenical copper for new auto radiators. A gross estimate is that of the 175 kkg/year of arsenic in copper scrap, 75 kkg/year reports in new radiators (along with 100 kkg/year of new replacement arsenic), while 100 kkg/year is dissipated in other copper alloy or is removed via electrolytic refining.

In summary, the flow of arsenic in the nonferrous metals industry is estimated as follows:

Additions of New Arsenic	
Retained in Primary Zinc	5 kkg/year
Retained in Primary Lead	20 kkg/year
Added to Lead for Lead Shot	60 kkg/year
Added to Lead for Bearing Metals	25 kkg/year
Added to Lead for Batteries, Cables	495 kkg/year
Retained in Primary Copper	43 kkg/year
Added to Copper for Admiralty Brass	7 kkg/year
Added to Copper for Auto Radiators	100 kkg/year
Total New Arsenic in Nonferrous Metals	700 kkg/year

Old Arsenic Recycled via Secondary Metals

In Bearing Metals	150 kkg/year
In Battery and Cable Lead	375 kkg/year
In Auto Radiators	75 kkg/year
Total Old Arsenic in Nonferrous Metals	600 kkg/year

Arsenic Losses in Nonferrous Metal Processing

Air Emissions, Secondary Lead Blast Furnaces	130 kkg/year
Land-Destined Slag, Secondary Lead Blast Furnaces	300 kkg/year
Total Arsenic Losses	430 kkg/year

Arsenic Dissipated in Nonferrous Metals

By Difference, New Arsenic Less Losses	325 kkg/year

An alternate method of accounting is by individual end items of alloys containing arsenic (kkg/yr):

End Items	Arsenic In End Items	Arsenic Reclaimed	New Arsenic Added	Arsenic Lost in Processing
Lead Shot	60	0	60	0
Lead Bearings	175	150	25	0
Lead Batteries	760	700	430	370
Lead Cables	110	105	65	60
Total Lead Items	1,105	955	580	430
Copper Radiators	175	75	100	0
Heat Exchangers	7	0	7	0
Total Copper Items	182	75	107	0
Total Pb & Cu Items	1,287	1,030	687	430

Phosphate Rock

Arsenic is a common trace constituent of phosphate rock, and occurs as adsorbed in ions on colloidal iron oxide rather than as a substitute for phosphorus in the fluorapatite. A statistical analysis of 51 commercial Florida pebble phosphates indicated a direct linear correlation between arsenic and iron in the rock, with arsenic varying from 3 to 15 ppm at a ratio of As/Fe of 800 ppm.(124) Reported values for the phosphorus, arsenic, and iron content of commercial phosphate rocks are tabulated in Table 10.

These data may be summarized by the following ratios:

	As/P_2O_5, ppm	As/P, ppm	As/Fe, ppm
Florida Pebble, Rock	45	100	1,370
Tennessee Rock	82	190	1,370
Western Rock	230	520	7,900

The quantities of marketable phosphate rock in 1972, the corresponding quantities of arsenic in the rock and the breakdown of phosphate and contained arsenic by consumption patterns are shown in Table 11.

The arsenic in phosphate rock follows the phosphorus quantitatively, whether the wet process for phosphoric acid (i.e., acidulation of the rock) or the furnace process (reduction to elemental phosphorus) is followed. In Table 11, the "non-agricultural" uses are those derived from the furnace process. Arsenic is intentionally removed from food-grade phosphoric acid by precipitation with Na_2S or NaHS followed by filtration; and arsenic is removed in the manufacturing processes for phosphorus pentasulfide phosphorus trichloride, and phosphorus oxychloride.(77,123) It is estimated that the arsenic removed (and disposed of on land) amounts to all of the 60 kkg/year associated with food-grade phosphoric acid plus half of the 60 kkg/year associated with miscellaneous uses. Conversely, all of the 293 kkg/year of arsenic associated with fertilizer, the 32 kkg/year

Table 10

Arsenic in Commercial Phosphate Rock

	Ref.	P_2O_5, %	Fe_2O_3, %	As_2O_3, %
Florida land pebble	13	30-36	0.7-2.6	10-50
	12			5-30
	124			22
	124			9
Tennessee brown rock	13	30-36	2.2-3.4	20-40
	12			7-75
Western rock	13	27-36	0.5-2.1	10-150
	12			6-140
	124			63-200

Table 11

Production, Conversion, and Consumption of Phosphates

	P_2O_5 Quantities, Metric Tons/Year	Arsenic Quantities, Metric Tons/Year
Florida Rock Produced	9,960,000	448
Used as Domestic Fertilizer	5,450,000	245
Used for Animal Feed	350,000	16
Exported	4,160,000	187
Tennessee Rock Produced	510,000	42
For Non-Agricultural Uses	510,000	42
Western Rock Produced	1,170,000	268
Used as Domestic Fertilizer	210,000	48
Used for Animal Feed	70,000	16
Exported	70,000	16
For Non-Agricultural Uses	820,000	188
Total Rock Produced	11,640,000	758
Total Used as Domestic Fertilizer	5,660,000	293
Total Used for Animal Feed	420,000	32
Total Exported	4,230,000	203
Total for Non-Agricultural Uses	1,330,000	230
Used for Detergents	630,000	110
Used for Food Products	350,000	60
For Miscellaneous Uses	350,000	60

associated with animal feeds, the 110 kkg/year associated with detergents, and the remaining 30 kkg/year associated with miscellaneous uses, remains with the phosphate products and is dissipated with these products.

The consumption of fertilizers is expanding at a 5 to 7 percent growth rate in North America:(125)

1965	3.6 million metric tons P_2O_5/year
1970	5.0
1975	6.3
1980	8.0

Hence, the arsenic associated with phosphate fertilizers is expected to grow to 410 metric tons per year by 1980.

Arsenic in household detergents and presoaks was measured at concentrations ranging from 2 to 59 ppm.(126) The production of sodium tripolyphosphate for the detergent industry has been cut back over the past several years because of the environmental concern over phosphorus in wastewaters.

Sludges from Municipal Sewage Treatment and Municipal Water Treatment

Some of the arsenic in domestic sewage concentrates in the treatment plant sludge, in a similar fashion as other metals. At one secondary treatment plant, the arsenic in the thickened waste sludge was at a concentration of 61.4 μg/l; at an assumed 8 percent solids content, the sludge solids would have contained 0.75 ppm arsenic.(127) If the per capita dry sludge solids quantity is 0.091 kilograms per day, and if 120 million people are served by municipal sewage treatment plants, then the quantity of arsenic in sewage sludge is 3.0 metric tons per year, contained in a dry sludge quantity of 4 million kkg/year.

The arsenic emission factor for sludge incineration is reported as 0.01 kg per kkg of "sewage and sludge".(10) Assuming a solids concentration of 20 percent in dewatered sludge (feed to an incinerator), the emission factor is equivalent to an arsenic concentration in dry sludge of 2 ppm, and it implies that all of the arsenic is volatilized. Since about one-third of all sludge is incinerated, one kkg/year of arsenic is emitted to the air and 2 kkg/year is applied to land.

It was also determined that municipal water treatment plants remove arsenic. Cold-lime softening removed 85 percent of the arsenic in raw water, from a raw concentration of 3.1 ppb.(126) If the per capita water use is 200,000 liters per year, or 24 x 10^{12} liters per year for 120 million people; then at a removal rate of 2.7 μg/liter the quantity of arsenic in water treatment sludge is 65 metric tons per year.

Sulfur Deposits

Based upon one reported value of less than 10 ppb of arsenic,(128) it is apparent that Frasch process sulfur does not contain appreciable arsenic.

Borax and Boric Acid

While boron is not an extremely rare element, few commercially attractive deposits of boron minerals are known. It is estimated that about half of the commercial world boron reserves, estimated at about 72 million tons of boron, are in southern California as bedded deposits of borax (sodium borate) and colemanite (calcium borate), or occur as solutions of boron minerals in Searles Lake brines. The United States is the largest producer of boron, supplying 71 percent of the free world demand, and also the largest consumer, requiring about 36 percent of the world output. The U.S. production of boron minerals and compounds has averaged 1.07 million metric tons per year in the 1972-1974 time period; the corresponding quantity of B_2O_3 is 580,000 metric tons per year. Approximately 80 percent of the U.S. production is from ores, and the remainder is from saline brines.(18,70)

The borate deposit in the Kramer district of California is a large, irregular mass of bedded crystalline sodium borates ranging from 80 to about 1,000 feet in thickness. Borax, locally called tincal, and kernite are the principal minerals. Shale beds containing colemanite and ulexite lie directly over and under the sodium borate body.

United States Borax and Chemical corporation mines the ore by open-pit methods. It is blended and crushed to produce a minus 3/4 inch feed of nearly constant boric oxide (B_2O_3) content. Weak borax liquor from the refinery is mixed with the crushed ore and heated nearly to boiling point in steam-jacketed tanks to dissolve the borax. The concentrated borax liquor goes to a series of thickeners, is filtered and pumped to vacuum crystallizers. One of the crystallizers produces borax pentahydrate, and the other produces borax decahydrate. The pentahydrate is used for boric acid manufacture.

Arsenic is present as a sulfide (Realgar) in the mine run ore and associated shales. The occurrence is intermittent, and a given ore horizon can vary from 0 to over 1,000 ppm of arsenic. The residue from the digested ore amounts to 800 kg per metric ton of borax products, and contains approximately 45 ppm of arsenic.(123) On the basis of 860,000 metric tons per year of borax derived from ore, the quantity of wastes is 690,000 kkg/year, and it contains 31 metric tons per year of arsenic. These wastes are deposited in ponds, and covered with water to prevent blowing dust. Since there is no ground water in the remote desert area, there is no likelihood of contamination derived from percolation. Process wastewaters are evaporated in ponds.

Sodium borates are also extracted from Searles Lake brines by Kerr-McGee Corporation whose primary products are soda ash, salt cake, and potash. Searles Lake is a dry lake covering about 34 square miles in San Bernardino County, California. Brines pumped from beneath the crystallized surface of the lake are processed by carbonation, evaporation, and crystallization procedures, producing an array of products including boron compounds.

The salt body is actually two deposits separated by a layer of muds, and each deposit contains brines of different compositions. However, both the upper structure brine and the lower structure brine contain 0.05 percent Na_3AsO_4, equivalent to 180 mg/l elemental arsenic.(129) The total brine processed is about 12×10^9 liters per year,(129) so that the contained arsenic is 2,160 metric tons per year. The depleted brines, plus added process waters, are returned to the lake; almost all of the arsenic in the brine extracted from the lake is directly returned to the lake in the depleted brine. The only arsenic extracted from the brines is that unintentionally carried as an impurity in the products of the operation.

Boric acid is made by acidulation of borax pentahydrate:

$$3Na_2B_4O_7 \cdot 5H_2O + 3H_2SO_4 = 12H_3BO_3 + 3Na_2SO_4$$

From the acidulator, the boric acid solution is fed to a vacuum crystallizer where boric acid crystals are formed, and then to a filter. The sodium sulfate is removed in the filtrate, and the technical grade boric acid is dried and packaged. The technical grade product can also be diverted upstream of the final drying step, redissolved, crystallized, filtered and dried to produce a higher purity product. Sodium sulfate is a co-product and most of the wastes are waterborne. The combined waste liquors from several filtration and centrifugation steps amount to 2,800 liters per metric ton of boric acid product, and contain 36 grams of arsenic. The quantity of borax used as a raw material is 1.72 metric tons per metric ton of boric acid product.(123) Since the production volume of boric acid is 110,200 metric ton of boric acid product, and contain 36 grams of borax is used for this purpose, and the raw wastewaters contain 3.9 metric tons per year of arsenic. At present, the arsenic-containing wastewaters are discharged, but the impact of effluent discharge limitations should cause arsenic wastes to be diverted to land disposal by 1977.(123)

Furthermore, if it is assumed that the arsenic in boric acid wastewaters represents all of the arsenic in the borax raw material, then the concentration of arsenic in the borax is 21 ppm. Since the residue from borax manufacture amounts to 800 kg per kkg of borax and contains 45 ppm of arsenic, then the material balance of arsenic is as follows:

	Total Quantity, kkg/year	Arsenic Concentration, ppm	Arsenic Quantity, kkg/year
Borax Ore Mined	1,550,000	32	49
Borax Product from Ore	860,000	21	18
Residue from Ore	690,000	45	31
Borax Product from Brines	210,000	21	4
Total Borax Product	1,070,000	21	22
Borax Consumed for H_3BO_3	190,000	21	4*
Other Borax Products	880,000	21	18

*This arsenic is subsequently a waterborne residual from H_3BO_3 manufacture.

Iron Ore

Sedimentary iron ore has been reported by U.S.G.S. to contain 400 ppm arsenic.(130) Although little substantiating data has been found, this value is consistent with the pattern of coprecipitation of arsenic with hydrous iron oxides. For example, the As/Fe ratio in Florida phosphate rock deposits was previously shown to be 1,370 ppm; applying this ratio to crude iron ore with an iron content of 37 percent results in an extrapolated arsenic concentration of 500 ppm in the crude ore.

On the other hand, the very lack of substantiating data for the concentration of arsenic in iron ore leads one to question the validity of this one reported value of 400 ppm. In comparison, the phosphorus content is universally reported; it has averaged 400 ppm for Lake Superior ores in the 1970-1972 period.(70) The wastewaters from iron mines and from iron ore processing have been characterized in terms of almost 20 constituents, without mention of arsenic.(73)

Arsenic was discussed as a minor constituent of iron ore in a United Nations survey:(131) "Arsenic in excess of 0.1 percent is uncommon in iron ores; when present, it is usually found in brown hematites as arsenopyrites (FeAsS), loellingate ($FeAs_2$) and scorodite ($FeAsO_4 \cdot 4H_2O$)." Based upon the U.S.G.S. and the U.N. references, the arsenic content of iron ore will be assumed to be 400 ppm for the purposes of this study, although more effort should be expended in verifying this concentration level.

For the past five years (1970 through 1974), the average usable iron ore statistics have been as follows:(18,70)

Production	84.6 million metric tons/year
Imports for Consumption	43.0
Exports	3.1
Consumption, Total	134.5

Based upon the above level of consumption of iron ore in blast furnaces and upon an arsenic concentration of 400 ppm, the quantity of arsenic entering the U.S. blast furnaces is 54,000 metric tons per year.

Arsenic acts very much like phosphorus in the blast furnace; it is completely reduced forming non-volatile iron arsenide (FeAs) and iron diarsenide ($FeAs_2$), and reports in the pig iron.(131,132) In 1970 to 1974, the average U.S. pig iron production was 83.0 million metric tons per year,(18,70) so that the 54,000 metric tons per year of arsenic would result in a concentration of 650 ppm (0.065 percent) in pig iron.

Of this pig iron, 78.0 million metric tons per year was consumed in steelmaking, while 5.0 million kkg/year was consumed for cast iron products (2.4 million in cupolas and 2.6 million in direct castings). The arsenic retained in cast iron would be 3,300 kkg/year. In the basic steelmaking processes using pig iron (basic oxygen and basic open hearth), most of the arsenic as well as the chemically-similar phosphorus is removed by the lime flux, and reports in the slag as calcium arsenate. The phosphorus content of pig iron is in the range of 0.15 percent, while the corresponding content in steel is 0.035 percent.(60) By analogy, it is assumed that the arsenic content of pig iron, 0.065 percent, is reduced to 0.015 percent in basic steelmaking.

Some of the arsenic lost in steelmaking would be in the steelmaking dusts (as a consequence of entrainment of solids rather than as a result of volatility). In 1972, the basic oxygen process consumed about 56 million kkg of pig iron while the open hearth process consumed about 22 million kkg.(70) The uncontrolled dust emission factors are 25.5 kg/kkg steel produced for the basic oxygen furnace and 4.15 kg/kkg steel produced for the open hearth.(133) Moreover, the 1972 steel production quantities were 67.6 million kkg for the basic oxygen and 31.7 million kkg for the open hearth.(70)

If it is assumed that the arsenic in the uncontrolled dust emissions is at the same concentration level as it is in the steelmaking charge, the following may be derived for the steelmaking processes:

	Basic Oxygen	Open Hearth	Total
Arsenic In Pig Iron, kkg/yr	36,400	14,300	50,700
Dust/Pig Iron, kkg/kkg	0.0308	0.00599	—
Arsenic In Dusts, kkg/yr	1,100	100	1,200
Arsenic In Slag, kkg/yr	25,200	9,400	34,600
Arsenic In Steel, kkg/yr	10,100	4,800	14,900
Total Dusts, kkg/yr	1,720,000	132,000	1,852,000

If a 99 percent dust collection efficiency is assumed, then the collected dusts would contain about 1,200 kkg/year of arsenic while the air emissions would contain 12 kkg/year of arsenic.

In past years, the collected dusts from steelmaking furnaces (which contain iron oxide) were sent to the sintering plants along with ore fines, coke breeze, limestone and recycled material from various mill processes. The purpose of the sintering process is to form larger agglomerates from the fines for recycle to the blast furnace. However, the sintering operation has been under recent attack because of its poor record of air pollution, and the recent trend has been to dispose of furnace dusts as landfill rather than to recover the iron values by sintering and recycling. Little is presently known of the environmental hazards of land-destined dusts containing arsenic, which of course involve much more arsenic than the arsenic emitted to the atmosphere.

The 2.4 million metric tons per year of pig iron which is used for cast iron production via cupola and similar furnaces is augmented by 14.8 million metric tons per year of scrap feed, for a production level of 17.2 million metric tons per year.(70) EPA reports an arsenic uncontrolled emission factor for cast iron production of 0.007 kg per metric ton of metal charged,(10) which implies a total arsenic emission of 120 metric tons per year from these sources. This amounts to one percent of the arsenic in the metal charged (at 650 ppm), 11,200 kkg/year. The emitted arsenic may be partially due to dust entrainment, and it may also be due to volatization of As_2O_3 from iron arsenite (the intermediate stage of reduction between iron arsenate and iron arsenide). The arsenate and the arsenide are both non-volatile, but the arsenite is volatile.(131) The high level of arsenic in the cupola dusts, 0.7 percent,(10) suggests that volatility plays a significant role.

Of the uncontrolled emissions of 120 kkg/year of arsenic from cast iron furnaces, an estimated 20 kkg/year is released to the atmosphere, with the remaining 100 kkg/year collected and disposed of on land. The relatively low collection efficiency is based upon the implied volatility of the arsenic emissions

The slag from steel-making furnaces is widely used, as the following 1972 data indicate:(70)

Use	Metric Tons/Year
Railroad Ballast	1,200,000
Highway Base or Shoulders	3,240,000
Paved-area Base	1,610,000
Misc. Base or Fill	1,750,000
Bituminous Mixes	510,000
Agricultural	100,000
Other Uses	800,000
Total	9,210,000

It should be emphasized that the estimate of the quantity of arsenic in steel slag (34,600 metric tons per year) is a very rough one, indeed. In addition, no information was obtained on the potential for arsenic leaching from slag in the uses typified by the above data.

Manganese Ores

Analyses of three typical manganese ores are as follows:(134)

	Brazil	Brazil	Mexico
Mn, %	50	48	47
Fe, %	4.1	5.2	1.8
P, %	0.07	0.09	0.01
As, %	0.18	0.15	0.25

An average value of 0.20 percent arsenic will be used in this analysis.

All of the manganese ore (with 35 percent or more Mn) consumed in the U.S. is imported, principally from Africa and Brazil. The U.S. government stockpiles manganese ore, and in recent years has released significant quantities to industry. There is a sizable domestic production of manganiferous ore (5 to 35 percent Mn). The quantities involved are shown on Table 12. At an average level of domestic industrial consumption of 2.0 million metric tons per year, the quantity of arsenic involved is 4,000 metric tons per year.

The smelting of manganese ore to produce manganese ferroalloys (ferromanganese, silicomanganese, and spiegeleisen) is generally accomplished in blast furnaces or electric furnaces, with technology very similar to iron and steel manufacture.(17,135) Although little data is available on the fate of the arsenic in the smelting of manganese ores, an analogy may be drawn to the transport of the chemically-similar phosphorus: 60 percent of the phosphorus in the ore passes into the ferroalloy, 30 percent passes into the slag and 10 percent escapes with furnace gases.(135) Since about 90 percent of the manganese ore is consumed in ferroalloy production, the fate of the arsenic is estimated (by analogy with phosphorus) as follows:

Retained in ferroalloys, consumed in iron and steel	2,160 kkg/year
In slag from ferroalloy furnaces	1,080 kkg/year
In collected dusts from furnaces	350 kkg/year
Air Emissions from furnaces	10 kkg/year
Total	3,600 kkg/year

The remaining manganese ore is used for making carbon-zinc and alkaline manganese dioxide dry cell primary batteries, and for use in the chemicals and glass industries. In 1972, 208,900,000 alkali batteries were produced by seven plants, with a total battery weight of 14,087 metric tons (an average of 67.3 grams per battery). Of the total battery weight, 27.4 percent is manganese

Table 12

Manganese Ore Statistics

Year	Manganese Ore, kkg/year			Manganiferous Ore Produced, kkg/yr
	Imported	Govt Stockpile Releases	Consumption	
1968	1,660,000		2,020,000	220,000
1969	1,780,000		1,980,000	390,000
1970	1,570,000	140,000	2,140,000	330,000
1971	1,740,000	110,000	1,950,000	180,000
1972	1,470,000	200,000	2,110,000	130,000
1973	1,370,000	170,000	1,940,000	
1974	1,090,000	910,000	1,630,000	

dioxide,(136) implying that 3,870 metric tons of manganese dioxide were consumed in 1972. At an arsenic concentration of 0.2 percent, the quantity contained is 7.75 kkg/year. These alkaline dry cells have found wide usage in flashlights, camera equipment, battery-powered toys, radios, tape recorders, etc.; since the alkaline cell yields an improved performance (at higher cost) over carbon-zinc cells, particularly for heavy or continuous current drains.

The carbon-zinc batteries produced in 1972 amounted to 95,920 metric tons. Manganese dioxide amounts to 61.5 percent of the battery weight, implying a consumption of 58,900 metric tons per year of MnO_2.(136) The MnO_2 is used as a depolarizer in conjunction with ammonium chloride, zinc chloride, and starch to form the electrolyte. The carbon-zinc batteries are used for similar purposes as the alkaline battery, although larger industrial carbon-zinc batteries are also used. At an arsenic concentration of 0.2 percent, the quantity contained is 118 metric tons per year.

Hence, the total arsenic dissipated in primary batteries is 126 metric tons per year. The remainder, approximately 274 metric tons per year, is involved with chemical-grade manganese ore, and is dissipated in products such as hydroquinone or potassium permanganate. It appears that virtually all 400 kkg/year of arsenic in non-ferroalloy manganese ore is dissipated in end products.

In addition to manganese ore reserves, the potential for large-scale recovery of manganese nodules on the deep ocean floors has attracted intense U.S. and foreign attention. Ferromanganese nodules in the mouths of rivers and in bays in Lake Michigan contain 200 to 500 ppm arsenic.(137)

Fossil Fuels

The average arsenic content of domestic coal has been reported to be 5.44 ppm. Eastern coals contain 10 ppm arsenic and western coals 1 ppm.(9) The arsenic content of coal increases with increasing sulfur and iron pyrite content;(138) this observation is consistent with the sulfur contents of eastern (3 percent) and western (0.7 percent) coal.

The U.S. bituminous coal statistics, including a projection for 1980, in millions of metric tons per year, are:(18)

Year	Production	Exports	U.S. Consumption (total)	U.S. Consumption (electric power)
1970	547	64	468	290
1971	501	51	449	299
1972	540	51	469	317
1973	537	48	505	351
1974	535	55	490	355
1980	812	(54)	(758)	580

Based upon an annual consumption of 450 million metric tons and upon an average arsenic content of 5.44 ppm, the arsenic associated with coal is 2,450 metric tons per year. In a study of coal-fired power plants, 73 percent of the arsenic in the coal reported in the bottom ash and in the collected fly ash, while 27 percent (1.46 grams arsenic per metric ton of coal burned) was emitted to the air <u>after</u> dust collection.(9)

The data above also show that in 1974, 72 percent of the total coal consumed was for electric power generation. Of the remainder, 17 percent was consumed by coke plants, 11 percent by other manufacturing and mining industries, and only 1 percent was delivered by retail dealers.(18) The proportion for electric utilities is expected to increase by 1980. The coal consumed by coke plants is selectively the low-sulfur coal, so by inference the arsenic quantities should be small. Applying the above emission factor to the total coal consumption should therefore be a reasonable procedure. The arsenic emitted to the atmosphere is estimated to be 650 metric tons per year; while the arsenic in bottom ash and in collected fly ash, destined for land disposal, is estimated to be 1,800 metric tons per year. The arsenic in the ash is, in general, partially mobilized into the environment via dusting and via leaching.

Of major importance in this estimate of arsenic emissions from coal is the projected increases in coal utilization due to the energy situation. The foregoing table lists the rather stable coal statistics for the past five years, but the 1980 projection reflects an annual growth rate of over 6 percent. The impact is that the domestic consumption in 1980 is expected to be around 760 million metric tons. Hence, the arsenic quantity could be increased to about 4,100 metric tons per year (1,100 kkg/year in air emissions and 3,000 kkg/year in land-destined wastes).

The growth of coal consumption is expected to continue well past 1980; the U.S. recoverable reserves are estimated to be 394 billion metric tons.

Much research is currently underway in developing coal conversion processes (synthetic oil and synthetic low-and-high-Btu gas). The EPA is actively investigating the fate of the heavy metals in these conversion processes. In one preliminary study(139) of a high-Btu gasification process, starting with Pittsburgh No. 8 coal containing 9.6 ppm of arsenic, 22 percent of the arsenic was volatilized in the first stage (430°C and 1 atmosphere), an additional 25 percent in the second stage (650°C and 74 atmospheres), and an additional 18 percent in the third stage (1000 °C and 74 atmospheres), leaving 35 percent of the original arsenic in the residue. As expected, the more volatile trace elements (Cd, Hg, Pb, As, Se) wound up primarily in the product gas, while most of the less volatile trace elements (Cr, Ni, and V) remained primarily in the residues.

A projected implementation of coal gasification is that by 1990 the U.S. will have the capacity to process 220 million metric tons of coal per year.(139) The above preliminary data indicating that two-thirds of the arsenic is volatilized (and therefore would become air emissions upon combustion of the synthetic gas) is the incentive for research to remove this arsenic.

The average arsenic content of foreign and domestic crude oils and of residual oil was 0.14 ppm.(9) At an average specific gravity for crude oil of

0.85 kg/liter, the volumetric arsenic concentration is 0.12 mg/liter. The total domestic demand for petroleum products is as follows:(18,70)

1970	0.853×10^{12} liters/year
1971	0.882
1972	0.951
1973	1.000
1974	0.982

Hence, the arsenic in consumed petroleum amounts to 120 metric tons per year. In 1972, the consumption pattern was as follows:(70)

Gasoline	39.2%	
Jet Fuel	6.4	
Other Light Fuels	11.2	
Distillate Fuel Oil	17.8	
Residual Fuel Oil	15.5	
Total Fuels		90.1%
Chemical Feedstocks	3.8	
Asphalt, Road Oil	1.9	
Misc. Products	4.2	
Total Non-Fuel		9.9%

For the 90 percent of the total petroleum that is burned, all of the arsenic is in the form of air emissions; this amounts to 108 kkg/year. The remaining 12 kkg/year of arsenic may be assumed to be dissipated in end products.

Oil shale is projected to fill a small but significant fraction of the U.S. energy demand:(140)

Year	Total U.S. Energy Demand, 10^{18} joules/yr	Oil Shale Production/Yr		Percent of Demand filled by Oil Shale
		10^9 Liters Oil	10^{18} joules	
1975	83	0	0	0
1980	98	16	0.6	0.6
1985	120	52	2.0	1.7
1990	140	70	2.7	1.9
1995	170	87	3.4	2.0
2000	200	105	4.0	2.0

This projection is highly dependent, of course, upon the relative economics of oil shale vs. petroleum; water availability is a serious constraint. The arsenic in oil shale has been reported to be at a level of 82 ppm. Since the expected oil recovery is about 140 liters per metric ton of oil shale,(140) the quantities of mined oil shale and of arsenic corresponding to the above projections of oil production are:

Year	Oil Shale Mined, Million kkg/year	Arsenic In Oil Shale, kkg/year
1975	0	0
1980	115	9,000
1985	370	30,000
1990	500	41,000
1995	620	51,000
2000	750	62,000

The oil shale will be mined with underground mining methods, since the amount of overburden is prohibitive for surface mining. It is anticipated that the spent shale residue will be disposed of on land in 80-meter-deep piles. Once shale has been retorted, the organic binding is destroyed and the rock loses its strength and is easily crushed, thereby exposing soluble minerals to leaching actions.(140)

It appears likely that while some of the arsenic would be in the recovered oil, process wastewaters, or process gases, most will probably be retained in the spent shale residue as non-volatile arsenates. Hence, the primary concern over arsenic may be the possibility for erosion, leaching and runoff. If slurry transport of processed shale is employed, the mobilization of arsenic would be accelerated. In order to protect surface and ground waters, control measures such as impermeable basin liners and surface revegetation would likely be employed.

It is also possible that any organic arsenic originally in the oil shale would be volatilized in reducing atmospheres in the retorts to arsine or to methyl arsines.

Geothermal Energy

Geothermal waters, such as the waters of hot springs, contain much more arsenic than the average of one ppb of normal fresh water. Extreme concentrations up to 13.7 ppm have been reported for hot springs,(130) and it has been considered that hot springs and volcanic exhalations contributed much of the arsenic now present in the sediments and sedimentary rocks of the earth's crust.(22) A report of the composition of geothermal fluids from three locations makes no mention of arsenic, although 20 other components were reported at concentrations in the 100 ppb range.(140) For the purposes of this study, arsenic concentrations of 10 ppb and of 1 ppm will be investigated.

Geothermal energy (like oil shale) is projected to fill a small but significant fraction of the U.S. energy demand:(140)

Year	Geothermal Energy Produced, Billion KWH/yr	Liquid Brought to Surface, Million kkg/yr	Arsenic In Liquid, kkg/yr At 10 ppb	Arsenic In Liquid, kkg/yr At 1 ppm
1975	4	8	0.08	8
1985	50	900	9	900
2000	400	14,000	140	14,000

In the above tabulation, the factors used were 40 kilograms of liquid per KWH for wet geothermal processes and 2 kg/KWH for dry processes.

Reinjection of the fluids into the subsurface geothermal reservoir, after the heat energy has been extracted, is the likely course that will be followed. In this event, none of the arsenic in the fluid (regardless of its concentration) should be mobilized into the environment.

SECTION VI

ARSENIC TOXICOLOGY

The medicinal potential of arsenic has been acclaimed for nearly 2500 years. Hippocrates (460 to 377 B.C.) is said to have treated ulcers and other disorders with realgar (As_2S_2, arsenic sulfide).(27) The toxic properties of arsenic have supposedly been known for at least 2000 years, and for the past 300 years, arsenic has found use as a poison for virtually all living things including animals, plants, humans, intestinal parasites, and the bacteria associated with such diseases as syphilis and sleeping sickness.(95) Arsenical compounds have, through the last few centuries, acquired reputations as stimulants and tonics; they have been considered at times to be specific remedies for anorexia, neuralgia, rheumatism, arthritis, asthma, chorea, malaria, tuberculosis, diabetes, and skin diseases. As recently as 1937, arsenical medicinals accounted for about two-thirds of the 12-thousand organo-metal medicinals used at that time.(27)

Pure metallic arsenic and arsenous sulfide have practically no toxic effect on plants or animals, probably because of their extremely low solubility in both water and body fluids. No toxic effects have been reported from the handling of elemental arsenic.(1) The most toxic of the arsenical compounds is arsine (AsH_3, hydrogen arsenite) and its methyl derivatives, mono-, di-, and trimethyl arsine, all of which are gases having a characteristic garlic odor. The toxicities of all other arsenical compounds fall between these extremes. From the standpoint of chemistry and toxicology, the important compounds of arsenic fall into three major categories:

1. Inorganic arsenicals - white arsenic (As_2O_3), arsenate (As +5) salts, and arsenite (As +3) salts.
2. Organic arsenicals - the trivalent (As +3) arsenicals generally have the greatest physiologic significance; they may be mono-, di-, or trisubstituted; biological action is a function of molecular structure.
3. Gaseous arsenic - arsine and the methyl derivatives of arsine.

The National Institute for Occupational Safety and Health estimates 1.5-million American workers are potentially exposed to arsenic. This number includes people working in arsenic and nonferrous metals (especially copper) production as well as agricultural personnel exposed to arsenical agricultural products (including insecticides, herbicides, fungicides, and feed additives). Other industries having exposure potential are glass manufacture, lead-acid battery manufacture, wood preservative production, and nonferrous alloying.(96)

Exposure Standards

The current Occupational Safety and Health Administration standard for atmospheric exposure to inorganic arsenic (defined by OSHA as arsenic and its inorganic compounds, except arsine) is 0.5 mg/m^3, averaged over an 8-hour period. The OSHA standards for lead and calcium arsenates are listed separately and are 0.15 and 1.0 mg/m^3, respectively. The current standard for arsine is 0.2 mg/m^3. These standards (except for arsine) are based on the 1968 ACGIH (American Conference of Governmental Industrial Hygienists) list of Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment.(97) The ACGIH standards were based on the controversial study by Dr. Sherman Pinto - then medical director of the American Smelting and Refining (ASARCO) plant in Tacoma, Washington - where he concluded that no conclusive correlation exists between arsenic exposure and respiratory cancer.(98,99) Pinto's study is discussed below.

OSHA has recently proposed new guidelines for workplace exposure to inorganic arsenic; the maximum exposure would be 0.004 mg/m^3 and an "action level" would be 0.002 mg/m^3. Workers must be provided with protective equipment at levels above the lower limit. Exposure limit for a 15-minute period would be 0.01 mg/m^3.(97,99)

Standards for exposure to airborne inorganic arsenic compounds have varied considerably over the past three decades. In 1943 the American Standards Association recommended a level of 0.015 mg/m^3. After WWII the War Standard of 0.15 mg/m^3 was used. In 1947 ACGIH adopted a maximum acceptable concentration of 0.1 mg/m^3, but in 1948 this was raised to 0.5 mg/m^3 which is the value now prevailing. In 1974, NIOSH proposed a new standard of 0.05 mg/m^3, but after Dow and Allied acknowledged studies indicating a possible link between exposure to arsenic and higher than normal cancer rates, the standard was reduced to the currently proposed levels stated above.(99,100) The proposed new standards have not been met with any enthusiasm by producers and users of inorganic arsenic. A spokesman for ASARCO has pointed out that the proposed new limit is 650 times lower than for vinyl chloride (on a mg/m^3 basis), and that though carcinogenicity has been proven for vinyl chloride, it has not been proven for arsenic.(101) (NIOSH, on the other hand, is convinced arsenic is carcinogenic; this is discussed further below).

The United States Public Health Service has established a recommended maximum concentration of 10 ppb (0.010 mg/l) and a maximum permissible concentration of 50 ppb (0.050 mg/l) for arsenic in public drinking water; both of these limits are well below the lowest reported concentration known to have resulted in chronic poisoning - 0.21 mg/l.(5)

Acute and Chronic Effects

Arsenic absorbed into mammalian bodies is excreted in the urine, feces, skin, hair, and nails, and possibly trace amounts are released through the lungs. Arsenic, even in low dosages, tends to bind to keratin in skin, hair, and nails; keratin is a class of fibrous proteins characterized by, among other qualities, a high content of sulfur-containing amino acids. Arsenic bound to keratin is a slow route of arsenic elimination - i.e., via release of the metabolically dead tissues; hair, skin, nails. Table 13 lists the "normal" arsenic content for various tissues and fluids of the human body.

The major route of arsenic elimination is urine. Arsenic can be detected in the urine of people with no known exposure to arsenic, apparently ingested in food (especially seafood) or through other low-level environmental sources. The urine of workers exposed to arsenic may contain, and usually does contain, much higher levels of arsenic, even though no other symptoms of exposure may be apparent. Vallee, et al, cites the "normal" urine level of arsenic as 0.002 to 0.150 ppm.(27) In the NIOSH document, <u>Criteria for a Recommended Standard . . . Occupational Exposure to Inorganic Arsenic</u>, reference is made

TABLE 13

NORMAL ARSENIC CONTENT OF HUMAN TISSUES AND FLUIDS
(ppm, unless otherwise specified)

	Reference					
	(27)	(107)	(29)	(4)	(96)	(111)
Whole Body	0.2 - 0.3					
Urine	0.003 - 0.150	4-210 mcg/ 24 hrs	0.015 - 0.06		0.02 - 0.13	0 - 0.1
Blood	0.1 - 0.64	0.03 - 0.13		0.2 - 1.0		0.1
Nails	0.087 - 4.0					
Hair	0.036 - 0.88					1.0

to a study of 756 urine specimens from 29 people having no known exposure; average level of concentration was 0.08 mg/l with 79 percent of the samples being below 0.1 mg/l. The highest levels were 2.0, 1.1, and 0.42 mg/l, attributed to seafood consumption. In another study of 26 adults and 17 children, the average arsenic content of the urine was 0.014 mg As/l.(96)

Seafood is generally considered the main source of arsenic for "unexposed" people. In one test to establish the relation of seafood to urine arsenic levels, three subjects with pretest levels of 0.01, 0.05, and 0.3 mg As/l were given lobster tail for lunch. Four hours later urine levels were 1.68, 1.40, and 0.78 mg As/l, respectively. Ten hours after eating, urinary levels were 1.02, 1.32, and 1.19 mg As/l, and after 24 hours the values were 0.39, 0.39, and 0.44 mg As/l. After 48 hours, the values were approaching the pretest levels.(96,100) Table 14 lists the arsenic content of various foods.

The excretion of inhaled arsenic has been studied experimentally.(96) Eleven terminal lung cancer patients inhaled the radioactive isotope As-74. Uptake and distribution were measured with a radiation counter. Within four days, the lung level of arsenic had decreased to only 20 to 30 percent of the initial level, and thereafter the rate of disappearance tapered off slowly. About 28 percent of the inhaled arsenic was released in the urine in the first day. By the end of 10 days, urinary and fecal excretion of arsenic was approaching zero, with 45 percent having been excreted in the urine and 2.5 percent in the feces. The remainder was assumed to have been deposited in the body, exhaled, or eliminated over a longer period.

Interpretation of urine arsenic levels with regard to previous exposure or to individual tolerance for arsenic is difficult. Urinary arsenic levels of exposed workers vary widely and levels above 4.0 mg As/l have been reported without apparent adverse effects; however, signs of mild systemic poisoning have been reported in a worker excreting only 0.76 mg As/l. It has been concluded that, while no relationship can be shown between urinary arsenic levels and evidence of poisoning, urinary arsenic levels may well be used as a check on the efficiency of control measures of arsenic in worker environments.(100)

Table 14

Arsenic Content of Various Foods

Food		Arsenic Content (ppm)			
	(118)*	(105)*	(27)*	(5)*	(119)*
Fish	0.1 - 15			0.1 - 1.0	
Haddock	2.17				
Kingfish	8.86				
Mollusca	1-68				
Clams	0.0 - 2.94	15.9			
Oysters	0.0 - 400 (most 1.0)	16.0	3		6 - 45
Smoked Oysters		45.8			
Crustacea	10 - 79				
Crabs	0.2 - 7.0	25.0			46
Lobsters	75	22.1		up to 200	37
Shrimp	0.3 - 7.7	19.9	42	up to 200	24
Shrimp Shells	15.3				
Pork Loins	0.06				
Pork Kidney	0.0				
Pork Liver	1.4 - 1.07				
Stewing Beef	1.3				
Chicken Breast	0.0				
Milk, evaporated	0.17				
Tea	0.89				
Rhubarb	0.48				
Corn	0.11				
Corn Oil	0.0				
Coffee	0.0				
Wine Yeasts			as high as 150 to 180		
Baker's Yeast			up to 17		
Egg Lecithin	0.0				
Puffed Rice	1.6				
Table Salt	2.71				
Butter					0.07
Sugar					0.15
Lettuce					1.14
Oranges					0.22
Lemons					0.50
Rice and Wheat Flour					0.96
Apples					0.08 - 0.60
Pears					0.40 - 0.60
Grapes					0.75 - 1.20

*References

Acute Effects

Symptoms of acute poisoning may occur as soon as 30 minutes after ingestion. Major early manifestations are burning and dryness of the mouth and throat, dysphagia, colicky abdominal pain, projectile vomiting, profuse diarrhea, and hematuria. Shock develops as a result of dehydration. If the patient survives, the recovery may be complicated by development of encephalitis, myelitis, nephritis, or dermatitis.(27,96)

The fatal dose of arsenic trioxide for man is 70 to 180 mg., although toxicity may result from much smaller amounts. Arsenical concentrations in blood, urine, hair, and nails increase from 10 to 100 times normal in instances of acute poisoning.(27) Table 15 is a summary of toxicities of various common arsenical compounds.

Arsine is the most toxic compound of arsenic; 250 ppm for 30 minutes has been shown to be a fatal dosage, and 3 to 10 ppm can cause poisoning symptoms in a few hours. Animals exposed for 3 hours a day to concentrations between 0.5 and 2 ppm have been shown to develop "blood changes" (unspecified) within a period of several weeks. Typical arsine poisoning cases result in hemoglobinuria, jaundice, and hemolytic anemia. Data on actual concentrations causing acute intoxication are lacking; however, post-event concentrations of 70 to 300 ppm, 5 ppm, and even as low as 0.5 ppm have been reported. Urine samples analyzed at early stages of intoxication have contained arsenic concentrations ranging from 0.5 to 2 mg/l with occasional higher values being reported. The recommended Threshold Limiting Value for arsine is 0.2 mg/m^3 (0.063 ppm) - less than half the present limit of 0.5 mg As/m^3 for other inorganic arsenicals.(104)

Arsine is the most dangerous form of arsenic and the most serious in terms of industrial hazard. It has been referred to as the most powerful hemolytic poison found in industry. Clinically, the resultant illness has sometimes been referred to as "acid fume poisoning" or as "toxic jaundice". Arsine is liberated whenever hydrogen is generated in the presence of arsenic; the element may be a contaminant of either the metal or the acid used in the production of hydrogen. Arsine evolution may also result from reduction of arsenious or

TABLE 15

TOXICITIES OF VARIOUS ORGANIC AND INORGANIC ARSENICAL COMPOUNDS

Compound	Test Subjects, Method of Intoxication	Dose (mg/kg)	Reference
<u>INORGANIC</u>			
Arsenic Acid	LD_{50} oral, rats	48 - 100	(52)
	LD_{50} oral, young rats	48	(103)
	LD_{50} oral, old rats	100	(103)
	LD_{50} oral, rabbits	8	(109)
Arsenic Pentoxide	LD_{50} i.v., rabbits	8	(109)
Arsenic Trioxide	LD_{50} rats	138	(103)
	LD_{50} oral, rats	15	(108)
	LD_{50} rats, mice	35 - 50	(105)
	LD_{100} oral, man	1 - 2.5	(52) (110)
	LD oral, man	~1.4	(111)
Calcium Arsenate	LD_{50} (animal not specified)	35 - 100	(52)
	LD_{50} oral, rats	20	
Lead Arsenate	LD man	10 - 50	(52)
	LD_{50} oral, rats	100	(105)
Potassium Arsenite	LD_{50} oral, rats	14	(109)
Sodium Arsenate	MLD i.p., rats	50	(103)
Sodium Arsenite	LD_{50} mammalian	10 - 50	(52)
	MDL i.p., rats	10	(109)
	LD_{50} oral, rats	75	(103)
<u>ORGANIC</u>			
Cacodylic Acid	LD_{50} young rats	830	(31) (109)
	LD s.c., dogs	1000	(109)
Monosodium Methanearsonic Acid	LD_{50} oral, rats	700	(108)
Disodium Methanearsonic Acid	LD_{50} oral, rats	1000	(108)
Calcium Acid Methonearsonate	LD_{50}	4000	(52)
Arsphenamine	LD_{100} i.v., rats	100	(105)
Carbasone (p-uridobenzenearsonic acid)	LD_{50} oral, rats	510	(109)
	LD_{50} oral, rats		
Sodium Arsanilate	LD s.c., mice	400	(109)

<u>Abbreviations:</u>

LD - lethal dose
LD_{50} - lethal dose for 50 percent of test animals
LD_{100} - lethal dose for 100 percent of test animals
MLD - minimum lethal dose
i.v. - intravenous
s.c. - subcutaneous
i.p. - intraperitoneal

arsenic acid by means of nascent hydrogen, from electrolysis of arsenious solutions, and from the action of water or dilute acid upon metallic arsenides. Dangerous quantities may even appear from the action of atmospheric moisture upon arsenical-contaminated metallic sulfides.(27)

Early symptoms of acute exposure include headache, anorexia, nausea, vomiting, and paresthesia. Chronic exposure may be manifested by dyspnea on exertion and palpitation resulting from the anemia. In large measure mortality from arsine results from massive hemolysis. Survivors of acute arsine poisoning usually regain a normal state after about two weeks, but residual ECG changes, consisting of elevated T-waves in the procordial leads, have been reported to persist for many months. If death occurs, it usually results from sudden heart failure and pulmonary edema. At autopsy, the mucous membranes and serous surfaces are found to be stained with hemoglobin, and myocardial and renal degenerative changes have been observed. Arsenic tends to accumulate in the liver (up to 15 ppm), but large amounts are also found in the lungs and kidneys.(27)

Chronic Effects

Polyneuritis and motor palsies may be the only manifestations of chronic exposure. As in lead intoxication, weakness is most likely to affect the long extensors of the fingers and toes. Arsenical neuritis is said to be more symmetrical, widespread, and painful than that seen with lead. Personality changes may be included in the neurologic effects, along with headache, drowsiness, memory loss, and confusion. Nerve biopsy specimens from neurologically affected patients show degeneration. Chronic intoxication can also result in increased salivation, hoarseness, cough, laryngitis, conjunctivitis, and abdominal pain. Trophic skin changes with a purplish-red hue and smooth shiny finger tips are frequently seen.(27)

The typical symptoms of severe chronic arsenicalism include nausea, vomiting, diarrhea, hot flashes, and progressive anxiety. Such symptoms might continue intermittently. In one study cited in the NIOSH Criteria Document,(96) a worker exposed to arsenic for several years experienced a gradual darkening of the skin, and a thickening and scaling of the skin on the soles of the feet. An almost constant pain and feeling of pins and needles appeared first in the feet and later in the hands. Muscular weakness became more apparent and the extremities became numb in a glove and stocking manner. By three years after the first symptoms, the skin of the trunk had darkened markedly, and there had been a gradual loss of vision and increased pain. Attacks of the initial symptoms continued to occur three or four times annually for ten years, until the patient was referred to specialists for management of severe heart failure and muscular dystrophy. At that time, abdominal accumulation of fluid was evident and severe ankle edema had developed. The patient was constipated except during the episodes of nausea and vomiting, when he had diarrhea. He was emaciated and had a diffuse tan pigmentation over the trunk. The palms and soles were hyperkeratotic and Mees lines were present on the nails. All sensory functions were diminished toward the extremities. The patient could not walk.

Urinary excretion of this patient was 0.140 mg/24 hours; the hair contained 20.7 mg As/100 g of hair. The white count was low (2,174) with a slight increase in monocytes. Both the EEG and ECG were normal. In an effort to increase urinary excretion of arsenic, British Anti-Lewisite (BAL) was administered but to no avail. After 3 months of hospitalization, functional use of the hands returned and the patient could walk with the aid of leg braces and crutches; urinary arsenic excretion was approximately 0.040 mg/24 hours. A follow-up at one year revealed little, if any, improvement in the neuropathy. Deep tendon reflexes were still absent and there was no proprioception beyond the knees or elbows. Pigmentation was still marked but the dermatitis cleared completely.(96)

In a study of six patients exhibiting chronic arsenicalism, the symptoms were, as above, nausea, vomiting, diarrhea, and peripheral neuropathy. In three cases there was pigmentation, and in three cases there was hyperkeratosis of the palms and soles. However, in two cases neither hyperkeratosis nor hyperpigmentation were observed. Average urinary excretion was 1.87 mg As/l, with a range of 0.348 to 3.46 mg As/l of urine. Arsenic in the hair averaged 4.88 mg As/100 g of hair. Various blood abnormalities were evident such as white cell counts of less than 1000 (in three of the cases) and, in three of four of the patients examined, and improper production red cells in the bone marrow. However, blood abnormalities disappeared within several weeks.

Individual tolerance to arsenic intoxication varies considerably. Certain persons have reportedly been able to tolerate doses as high as 20 mg of potassium arsenate three times daily without exhibiting signs of toxicity. The "arsenic eaters" of Europe are reported to ingest as much as 400 mg of arsenic trioxide once or twice a week without developing symptoms; and they experience no withdrawal syndrome.(27)

An allergic type of contact dermatitis is frequently seen where white arsenic is handled. This dermatitis may be eczematous, follicular, erythematous, or even ulcerative in character. In heavily exposed workers, mucous membrane irritation, rhinorrhea, conjunctivitis, pharyngitis, and laryngitis are seen as direct results of exposure to arsenic dust and are preventable with proper protective devices. Particulate matter absorbed into the nasal passages induces inflammation and may result in ulceration and slough of cartilage leaving a 3- to 8-mm punched-out area in the septum.(27)

Accidental poisoning of agricultural animals and wildlife by solid arsenicals is reported occasionally, and it produces clinical syndromes and pathologic findings analogous to those in man.(27)

The NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Inorganic Arsenic(96) makes reference to a 1945 study in which medical records of workers in an arsphenamine plant were reviewed. Five types of complaints were considered to be possible indicators of "subclinical or borderline arsenicalism".

Hyperkeratosis	- warts cracking, chapped, dry, or thickened skin

Gastrointestinal - upset stomach
nausea
vomiting
abdominal pain
anorexia

Central Nervous System - headache
dizziness
fainting

Optic Nerve - blurring or diminution of vision
spots before eyes

Peripheral Neuropathy - shooting pains in extremities
numbness, tingling, sudden loss of muscular power

Another symptom commonly associated with arsenicalism is hyperpigmentation. In one case cited in the NIOSH Criteria Document, 15 vinedressers and cellarmen having symptoms of chronic arsenicalism had vascular disorders in the extremities, and "all had varying degrees of hyperpigmentation and all but 2 had palmar and plantar keratoses". Cold hands or feet or both were common to all and apparently preceded the development of gangrene on the toes or fingers in 6 of the 15 cases.(96)

Electrocardiograms also show changes possibly associated with arsenic exposure. In a case where 170 soldiers had been chronically exposed to arsenic in their drinking water, electrocardiograms were prepared for 80 of the soldiers, 45 of whom displayed abnormalities. Six weeks after the first examination, repeat ECG's were obtained in 47 cases, and the abnormalities initially observed were absent or reduced. In another study of 192 vinegrowers suffering from chronic arsenicalism, 56 percent had normal ECG's, 15 percent showed deviation from the normal, but not sufficiently deviant to qualify as evidence of definite heart muscle damage, and 29 percent showed definite changes - however, of this portion approximately one-third (19 out of 55 men) of the ECG changes could also be attributed to age, arteriosclerosis, or other disease. For abnormalities in the remaining two-thirds (36 men), no possible causes other than arsenic poisoning could be detected. Follow-up examination showed a decrease in ECG abnormalities in proportion to other symptoms of arsenic poisoning. Attempts have been made to relate ECG changes to disturbances in serum electrolytes, but no relation has been found; the changes are considered to be due to a toxic effect on the heart muscle.(96)

Cirrhosis of the liver has also been associated with chronic arsenic exposure via prolonged use of Fowler's solution (a dilute solution of potassium arsenite previously used as a treatment for leukemia and various skin diseases). Use of Fowler's solution has also been linked with "generalized mottling and bronzing of the skin, palmar and plantar hyperkeratoses, ascites, and marked edema".

Among workers exposed to inorganic arsenic, especially as airborne dust, the chronic symptoms commonly found are perforation of the nasal septum, conjunctivitis, and pharyngitis. There is reportedly a large degree of skin sensitivity variation among arsenic workers; however, sensitivity of the skin to airborne inorganic arsenicals is very common in moist skin areas or in areas where rubbing or chafing of the skin occurs such as areas around the eyes and wrists, or in facial areas where a respirator is likely to rub against the skin. Blond and fair-skinned people have been reported as being especially sensitive to arsenically induced dermatitis.

In one study cited in the NIOSH Criteria Document, dust-in-air measurements were considered of limited value in predicting skin reactions, as were levels of arsenic in urine; however, based on a study of 127 patients, dermatitis was observed in 80 percent of those excreting 1 to 3 mg As/l and in 100 percent of those excreting more than 3 mg As/l.(96)

The most controversial aspect of chronic arsenicalism is cancer and the possibility that arsenic might be carcinogenic. Findings of excess cancer deaths among workers chronically exposed to airborne concentrations of various inorganic arsenicals have implicated inorganic arsenic as an occupational carcinogen. Results of a number of studies have especially shown arsenic trioxide, lead arsenate, calcium arsenate, and sodium arsenite to be suspect carcinogens.

In 1963, Pinto and Bennett analyzed the causes of death of 229 copper and arsenic smelter workers at ASARCO's Tacoma plant, and on the basis of the average urinary arsenic levels divided the workers into "exposed" and "non-exposed" groups. Pinto and Bennett concluded that there was no significant difference in the rates of cancer for the two groups. The findings in this study became the basis for the present Federal standards for inorganic arsenic exposure after they were accepted by the American Conference of Governmental Industrial Hygienists, which until 1970 was the only organization setting standards for exposure to dusts and fumes in the workplace. With the passage of the Occupational Safety and Health Act of 1970, Pinto's findings were still used as the basis for the still-prevailing standard of 0.5 mg As/m^3 of air.(98) However, substantial controversy has come to surround the Pinto study during the last few years.

In a 1972 study by Milham and Strong, urinary arsenic levels of children living near the Tacoma smelter were measured and correlated to the distance the children lived from the Tacoma smelter.(102)

> Blood lead and urinary arsenic levels of third- and fourth-grade children at Ruston School (located about 300 yards from the west border of the smelter complex) were compared to those of similar students at another elementary school about 8 miles away. Blood lead levels were essentially the same for the two groups of children, but arsenic urinary levels were considerably elevated among the Ruston children.
>
> Hair specimen containers were sent home with children at the end of the school year and were returned over the summer. Hair arsenic levels were very high for Ruston children, averaging over 50 ppm while the control school children averaged less than 3 ppm.
>
> A few weeks after the initial study, urines were sampled along three downwind traverses starting at the smelter stack and extending nearly 3 miles south and southwest. There was a decline in urinary arsenic levels with distance from the stack.

The findings of Milham and Strong suggest that Pinto's "nonexposed" group, since they did indeed work within the smelter complex along with the "exposed" group (who worked in the actual smelting operations, as opposed to office operations where the "nonexposed" group prevailed), probably had a substantial exposure to airborne arsenic trioxide dusts.

In 1969 Lee and Fraumeni(103) studied the mortality statistics of white male workers at the same ASARCO Tacoma plant for the years 1938 through 1963, and compared the results to the expected mortality rates for the general population of the state. "The excess of respiratory cancer was as high as eightfold among employees who worked more than 15 years and who were heavily exposed to arsenic; it showed a gradient in proportion to the degree of exposure to arsenic and sulfur dioxide. The findings support the hypothesis that inhaled arsenic is a respiratory carcinogen in man, but an influence of sulfur dioxide or unidentified chemicals, varying concomitantly with arsenic exposure, cannot be discounted". Lee and Fraumeni also noted that "among the specific causes of death, tuberculosis, respiratory cancer, diseases of the heart, and cirrhosis of the liver showed a significant excess over expectation", based on mortality-by-disease for the state as a whole. But, as they point out, it is difficult to separate the effects of combined exposure to both As_2O_3 and SO_2.

Animal experiments on the carcinogenicity of arsenic have generally given negative results. Studies of the co-carcinogenic effects of arsenates and arsenites with such materials as cotton oil, urethane, and dimethylbenzanthracene have also been negative.(11,105) However, in the summer of 1974, Dow Chemical Company and Allied Chemical Corporation acknowledged that workers in their inorganic arsenic pesticide plants were dying of lung cancer at 7 times the expected rate, and of lymph cancer at 6 times the expected rate. As a result, some officials in NIOSH are now comparing industrial exposure to arsenic to that of vinyl chloride.(96,98) Some 15 copper, lead, and zinc smelters ship their arsenic-containing flue dusts to the ASARCO plant at Tacoma where white arsenic is produced. In total, about 40 different industries use white arsenic in their manufacturing processes.(98)

The carcinogenicity of arsenic has not been proven in animal studies. Even in combination with known carcinogens, animals exposed to various compounds of arsenic in their drinking water showed no increase in cancer rate over that expected for the non-arsenical carcinogen alone. However, the relation between arsenic and cancer in humans is considered by some to have been proven, especially by studies of worker populations exposed to inorganic arsenicals. The proposed standards for arsenic exposure cited in the NIOSH Criteria Document are based on an assumed carcinogenicity of arsenic. The last two sentences of the Criteria Document state that "because of the seriousness of [cancer], prudence dictates that the standard should be set at least as low as 0.05 mg As/m^3. It is believed that exposure at this level should, at the minimum, significantly reduce the incidence of arsenic-induced cancer".(96) The proposed standards in the 1973 Criteria Document have since been further reduced to 0.004 mg As/m^3 with an action level of 0.002 mg As/m^3. In supporting the original proposed standard of 0.05 mg As/m^3, NIOSH cited as evidence of the carcinogensis of arsenic three epidemiological studies, two of which were made with respect to the ASARCO smelter in Tacoma, Washington, while the other study was performed on workers in an English sheep dip factory. One of the studies of the Tacoma smelting complex and environs is the Lee and Fraumeni study where they state:(103)

> Arsenic has been suspected by many investigators as a carcinogen in man, though there is no supporting evidence from animal experiments. Skin cancer appears to be a definite consequence of arsenic exposure among individuals exposed to inorganic arsenic in industrial dusts, medicinals, and drinking water. Less convincing is the clinical evidence suggesting that long-term exposure to arsenic may give rise to cancer of internal organs, notably the lung.

Lee and Fraumeni also point out in their study, "the greatest excess of respiratory cancer occurred among smelter workers with high exposure to arsenic accompanied by high or moderate exposure to SO_2. Although no studies implicate SO_2 as a carcinogen in man, possibly this agent enhances the supposed carcinogenic effect of arsenic or other substances. From laboratory experiments, inhalation of the known carcinogen benzo[a]pyrene, combined with the irritant SO_2 produced squamous cell carcinomas of the lung in rats, whereas inhalation of the carcinogen alone did not produce tumors. . . Our findings are consistent with the hypothesis that exposure to high levels of As_2O_3, perhaps in interaction with SO_2 or unidentified chemicals in the work environment, is responsible for the excessive number of respiratory cancer deaths among smelter workers".

In the NIOSH-cited study of the English sheep dip workers, SO_2 was apparently not involved in the worker exposure, "but the cancer mortality of the chemical workers was significantly higher [than the control group]".(96)

The latest proposed standards, still under consideration at this time, are based on the belief that exposure to airborne concentrations of inorganic arsenic compounds are "strongly implicated as a cause in occupational carcinogenesis".(97) Ten epidemiological studies are cited by OSHA as the basis for this strong implication. Six of the studies show evidence of excess lung cancer mortalities among worker populations having had exposure to inorganic arsenic compounds. The authors of the other four studies concluded that there was no significant excess of cancer mortalities among inorganic arsenic workers; however, in the analysis of three of these studies, both NIOSH and OSHA confirmed that excess lung cancer mortalities were involved, but were not observed due to inadequate study designs. (No definitive conclusions could be assigned to the fourth study.) "Most of the available studies, including the data submitted by Dow and Allied, do show significant excesses of lung cancer mortalities for workers exposed to a variety of inorganic arsenic compounds".(97) There is no evidence implicating the ingestion of organic arsenic as a cause of cancer.

Mode of Action

Trivalent arsenic can chemically combine with the sulfhydryl groups; such groups are commonly found in proteins. Enzyme deactivation can thus result from the affinity of arsenic for the sulfhydryl groups which enzymes contain.(5) It has been demonstrated that trivalent arsenical toxicity can be reversed by administering reduced thiol compounds, such as glutathione and cysteine. The combining of arsenicals with tissue proteins and enzymes has actually been shown to be accompanied by a loss of titratible sulfhydryl groups. It has also been shown that there may be a direct correlation between the number of sulfhydryl groups in an organism and its sensitivity to arsenical intoxication.(27)

Studies involving the mode of action of the arsenical war gas lewisite have resulted in the determination of a large number of enzyme systems sensitive to arsenicals. An excess of simple thiol protects a variety of biological systems against the toxic inhibition of both organic and inorganic arsenicals - but not uniformly throughout an organism; specifically a 200-percent monothiol excess fails to protect the cerebral pyruvate oxidase enzyme system from lewisite, although other enzyme systems are completely protected by smaller concentrations. Investigations of this problem determined that lewisite reacts with some proteins in such a way as to bind two thiol groups, forming a stable compound not freely reversible with monothiols. The protective action of various dithiol compounds was therefore studied, and one compound, dimercaprol (2,3-dimercaptopropanol, also known as British-Anti-Lewisite or BAL) was found to be an effective antidote, even for protection of the pyruvate oxidase system of the brain.(27,105)

In addition to the affinity of trivalent arsenic for tissue sulfhydryl groups, arsenic may interact with biologic systems through other means. Arsenate or arsenite may compete with or substitute for phosphate in certain enzymatic reactions.(27)

In animals a direct relation between toxicity and strength of binding to tissues has been shown for a large series of phenyl arsenoxide compounds. Less firmly bound compounds are excreted more rapidly, and are less toxic at comparable levels of administration. At dosages producing equavalent toxicity (e.g., LD_{50}) tryparsamide, phenyl arsenic acid, and phenyl arsenoxide result in comparable tissue arsenic concentration despite a 500-fold difference in absolute amounts of arsenic administered.(27)

Arsenic is said to be a physiologic antagonist of iodine. The addition of 0.02 percent arsenic to the diet of rats has been shown to more than double their iodine requirement.(96) A high incidence of goiter and cretinism has been reported among the so-called "arsenic eaters" of Europe and among dwellers in the endemic zones of arsenical intoxication in the Cordoba province of Argentine.(27

Arsenic is also an antagonist of selenium. Agricultural animals exposed to selenium toxicity through forage in seliniferous areas are protected by small amounts of arsenic (5 to 10 ppm) in their drinking water.(96) Tungsten is the only other element known to provide such protection against selenium.(27)

Inorganic arsenic does not cross the blood-brain barrier in humans, though it may do so in some anthropoids. In man and rats arsenic is transferred across the placenta. It appears in cows' milk, but not in rodent milk.(27)

The major toxicity of arsine is due to the hemolysis of the red blood cells, but the exact reason for this effect is unknown. It occurs only under aerobic conditions and involves only mature cells. Neither arsenic trioxide nor arsenic pentoxide has this effect. Guinea pigs cronically exposed to arsine (0.5 to 2 ppm) exhibit increased red cell fragility, leukopenia, and a rapid fall of red cells to a stable level, roughly 80 percent of normal. The toxicity of arsine and its clearance from the bodies of mice has been compared to that of sodium arsenite; where arsenite is cleared exponentially from the animal with less than 10 percent remaining after 24 hours, arsenic derived from arsine is cleared more slowly, with about 45 percent remaining after 24 hours.(27)

Oxidation State vs. Toxicity

Generally, but not invariably, inorganic arsenicals are more toxic than organic, and trivalent arsenic is more toxic than pentavalent. Pentavalent arsenic, probably because of its lower affinity for thiol groups in protein structures,(5) is excreted faster than trivalent arsenic, though evidence of rapid excretion of all arsenicals has been shown. Pentavalent arsenicals, "although physiologically inactive in this form", rapidly penetrate all parts of the body, including the central nervous system. They are excreted otherwise unchanged, but some tissues can reduce small amounts to trivalent arsenoxides, which can then damage otherwise inaccessible cells.(27,59) There is also evidence of <u>in vivo</u> oxidation from trivalent to pentavalent forms,(96) cited as a possible means of natural detoxification.(5) At least 15 strains of bacteria have been identified which can oxidize trivalent arsenic (specifically sodium arsenite) to pentavalent forms (arsenate); it is hypothesized that the bacteria somehow derive energy from the reaction.(5) Inorganic trivalent arsenicals are cited as being between 5(109) and 60(5) times as toxic as pentavalent arsenicals in humans.

While arsenites are 10 to 60 times more toxic to human and animals than arsenates, arsine is even more toxic than arsenites.(5) Methyl arsines are also extremely toxic; trimethylarsine is the gas which was discovered in the end of the last century to be the agent responsible for instances of mysterious deaths reported in damp homes in Europe. The volatile trimethylarsine gas was geing produced by the action of mold and dampness upon the arsenical-containing wallpaper pigments.(5,27)

The characteristic garlic-like odor of arsine and its methyl derivatives has been found in many industrial and agricultural settings, especially in metal-finishing industries where arsenically contaminated reactions between acids and metals take place.(27) Methyl arsines can only occur as a result of microbial activity in both aerobic and anaerobic environments.(5,106) Workers using cacodylic acid to control vegatation in forested areas have reported the characteristic garlic odor, within as little as 48 hours after the thinning operation and lasting for as much as three weeks.(107) Virtually nothing is known about the stability of methyl arsines with respect to oxidation in air and water.(5) However, although trimethylarsine is considered insoluble in water, it is significantly more soluble in hydrocarbons, which may account for its accumulation in certain organisms.(5) Paradoxically, arsenic in shrimp (probably as also in other marine life forms) is probably in the form of trimethylarsine, and when consumed by rats is excreted much more rapidly and is much less toxic than arsenic trioxide; this implies that trimethylarsine in food is much less toxic than in air.(5)

Organic vs. Inorganic Arsenicals

Methyl arsines are organic arsenicals but as such they are exceptions to the general rule that organic forms are less toxic than inorganic forms; in fact, they are as toxic as unmethylated arsine, AsH_3, which, as has been pointed out, is the most toxic arsenical compound. The general rule is that organic arsenicals are between 10 and 100 times less toxic than inorganic arsenicals.(105)

As pointed out above, the organic arsenical trimethylarsine, when eaten in shrimp meat, is not retained in the bodies of rats; it is excreted in the feces. Other organic arsenicals for which this is true are notably the four feed additives used to improve feed efficiency and growth rate of poultry and swine. These four aromatic arsenicals are arsanilic acid, 3-nitro-4-hydroxyphenylarsonic acid, 4-nitrophenylarsonic acid, and p-ureidobenzenearsonic acid. Table 16 lists the dosage levels and maximum allowable tissue levels for the compounds.

The metabolism of ingested arsenic from the arsenical feed additives has been investigated by a number of researchers. Chickens excrete arsanilic acid largely unchanged; there is no evidence it is converted into any other organic arsenical or to an inorganic form. Four-nitrophenylarsonic acid, however, is converted to arsanilic acid, and 3-nitro is partly converted to 3-amino-4-hydroxyphenylarsonic acid, but there is no evidence it is converted to an inorganic form. In both poultry and swine, a high percentage of ingested arsenic is excreted very rapidly. In a 5-day "balance trial" with growing sheep, 87 percent of all ingested arsenic was excreted. Tissue levels of arsenic in arsenically-fed animals drop to well within the FDA-established tolerance levels within the 5-day withdrawal period required before the animals go to slaughter. In a study of arsenically-fed chickens - 50 ppm of 3-nitro for 70 days - tissue levels of arsenic after 5- and 14-day withdrawal period were as follows:(59)

Tissue level after (ppm):

	70 days of feeding	5-day withdrawal	14-day withdrawal	Controls	FDA Tolerance
kidney	0.64	0.10	0.08	0.05	2.0
liver	1.26	0.43	0.19	0.08	2.0
muscle	0.04	0.01	0.02	0.02	0.5
skin	0.05	0.02	0.03	0.02	0.5

TABLE 16

Maximum Permissible Levels of Arsenicals in Animal Feeds and Maximum Permissible Levels of Arsenic in Animal Tissue (59)

Compound	Species	Maximum Feed Level	Maximum Tissue Arsenic Level
Arsanilic Acid	Poultry*	90g/ton (100 mg/kg)	0.5 mg/kg fresh, uncooked muscle 2.0 mg/kg fresh, uncooked by-products
	Swine	90g/ton (100 mg/kg)	0.5 mg/kg fresh muscle and by-products other than kidney & liver 2.0 mg/kg fresh, uncooked kidney& liver
3-nitro-4-hydroxyphenyl-arsonic acid	Poultry	45g/ton (50 mg/kg)	Same as arsanilic acid
	Swine	68g/ton (75 mg/kg)	Same as arsanilic acid
4-nitrophenyl-arsonic acid	Turkeys	170g/ton (187 mg/kg)	Same as arsanilic acid
p-ureidobenzene-arsonic acid	Turkeys	340g/ton (375 mg/kg)	Same as arsanilic acid

*Broilers, laying hens and turkeys.

SECTION VII

ASSESSMENT OF HEALTH HAZARD

Arsenic is the most well known of the toxic elements, but the magnitude of its reputation as a poison exceeds its level of potential hazard to the general population. The greatest threat of arsenic to public health is in those parts of the country where nonferrous smelting operations emit arsenic fumes which cause an overall increase in the local (up to 10 to 15 miles) environmental concentrations of arsenic.

Workers as well as people living in the vicinity of smeltering and refining facilities are potentially affected and it is now generally conceded by industrial producers and users of arsenic compounds that arsenic stimulates a higher incidence of cancer than is found in the general population.(99,112)

The atmospheric concentration of arsenic in the area near one smelting facility averages 2.3 $\mu g/m^3$ over a 24-hour period, which is greater than the new proposed OSHA standard of 2 $\mu g/m^3$ for an 8-hour period in the workroom environment. The 2.3 $\mu g/m^3$ exposure corresponds to an annual pulmonary absorption rate (based on 20 m^3 of air breathed daily, and an assumed 100-percent adsorption of the entrained arsenic) of 16.8 mg for each adult in the local population, to which is added, of course, the exposure from other sources such as food or water which may have been contaminated by local high concentrations of arsenic.

The current worker exposure standard is 0.5 mg/m^3, which corresponds to an annual pulmonary absorption of 3650 mg - more than 20 times the single lethal dose level of arsenic in the form of arsenic trioxide. At this current exposure level workers are experiencing increased rates of cancer.

Cancer is the biggest issue facing arsenic-dependent industries during the last decade. The carcinogenicity of arsenic has been an active matter of debate for more than half a century, and though industry is beginning to acknowledge the findings of independent researchers showing that arsenic-exposed workers face increased lung cancer risk,(99,112) the debate continues, largely because animal studies have not shown a relationship between arsenic and cancer. The premise of the proposed new OSHA standards for workroom concentrations of arsenic is that arsenic is a carcinogen.(96,97)

At the current levels of exposure, some workers experience dermatitis on the moist areas of their skin and in areas where chafing of the skin is common, such as the point of contact between face masks and the face. The tissues of the lung are constantly moist and they present a large surface area to arsenic-laden air. Arsenic in smelter polluted air is in the trioxide form, one of the most toxic of the inorganic arsenical compounds, and, because it is trivalent, it presents those hazards especially associated with the affinity of trivalent arsenical compounds for sulfur-containing proteins. The moist condition of the lung seems tailored to optimization of the toxic hazard of trivalent arsenic trioxide to the delicate lung tissues.

Local populations and workers are also exposed to arsenic in higher than natural concentrations in areas adjacent to industries producing arsenical pesticides and other products out of powdered arsenical raw materials which are subject to dusting and becoming airborne; but the geographic area of exposure is estimated as being 2 to 3 orders of magnitude less hazardous (in both geographic extent and atmospheric concentration) than areas adjacent to nonferrous smelting and refining facilities.

Persons living or working in areas where cotton is ginned face a possible exposure hazard from the airborne arsenical dusts generated by the ginning process. Incineration of cotton gin trash also releases arsenic to the local environment, though again, the amount is small in comparison to that released by smelting operations.(9) (There are approximately 3000 ginning facilities in the U.S., versus about 50 smelting and refining facilities.)

For the general population, the sources of arsenic exposure are mainly food and drinking water, neither of which presents a hazard. The arsenic content of seafood is higher than that of other foods but the arsenic is apparently of a form that is rapidly excreted via the kidneys.

A large portion of the population faces potential exposure through the use of arsenical pesticides, especially in the Texas-Oklahoma area where arsenic acid is widely used to desiccate cotton prior to machine harvesting ("stripping").

This level of exposure is approximately equivalent to that of city dwellers living in the range of fallout from coal-burning power plants.(9) (In one study of arsenic pollution from coal combustion, it was calculated that a "standard man" would breath about 0.5 mg of arsenic per year(27) - less than one one-hundreth of the amount necessary to produce a minimum single-dose toxic effect.)

Though arsenic has the reputation of being a cumulative poison, the human body does have mechanisms for controlling the body burden at moderate dose levels. Inorganic arsenic (trivalent) accumulates about 20 times as rapidly as arsenic which has been incorporated into such food organisms as shrimp, chicken, or swine. Arsenic is removed from the body mainly through the kidneys. If the dosage level is on the order of that experienced by smelter workers, then urine remains the main mode of arsenic loss, but the skin, hair, and nails accumulate excess arsenic which is eventually lost during normal tissue growth and replacement processes. There is some evidence of long-term storage in bones, but in no way does arsenic compare to such a material as cadmium which progressively accumulates in the kidneys, with virtually zero loss.

Arsenic has been compared to mercury as a water pollutant; both are subject to microbially-mediated chemical cycles involving methylation. But unlike methyl-mercury which is absorbed readily at progressively increased concentrations up the food chain, arsenic does not undergo such a biomagnification. Also, as mentioned above, arsenic in food organisms, even in high concentrations, does not present any health threat yet identified.(5,59,116)

The remainder of this section discusses in greater depth the health implications of arsenic in air, water, and food, and the methods by which, and sources from which, arsenic gets into these three important consumables. A discussion of soil-pesticide interactions and of crop uptake is also included.

Arsenic in the Air

Arsenic pollution of the air derives largely from three sources: Nonferrous metals smelting, coal combustion, and cotton trash incineration. Lesser sources include industrial operations where arsenical dusts are agitated into atmospheric suspension, emissions from pesticide applications (including evaporation processes), and emissions from the incineration of pesticide containers.

Atmospheric emissions of arsenic from agricultural operations are probably responsible for the largest geographic distribution of arsenic in the United States. However, coal, because it is used so widely as the energy source for many urban electric power plants, probably provides the largest population distribution of arsenic. The other emission sources, nonferrous smelting and cotton trash incineration, are largely local problems.

Pesticides

In agriculture, spray applications of arsenical pesticides and herbicides may produce potentially hazardous exposure for nearby personnel - workers as well as local populations. This is especially true in parts of the country where machine-stripped cotton is grown, as in Texas and Oklahoma. Arsenical herbicides control weeds in the early part of the crop growth and arsenical desiccants and defoliants are used to prepare the cotton plant for harvesting. Arsenically-desiccated cotton is grown almost exclusively in the Texas-Oklahoma region. Arsenically-defoliated cotton is grown largely in the 11 other cotton-producing states.

The National Inventory of Sources and Emissions: Arsenic - 1968(9) estimates that in 1968 the total atmospheric emissions of arsenic due to pesticides was 2973 kkg, including 17 kkg from cotton gins and 296 kkg from the incineration of cotton gin trash. The amount of arsenic used in pesticides has not changed very much in total amount since 1968. The increased use of arsenic acid in the preharvest desiccation of cotton matches closely with the decreased use of arsenic in other agricultural uses. The emissions factor given in the National Inventory for the burning of cotton gin trash is 7.7 kg/1000 bales of cotton ginned. For the 10,857,000 bales ginned in 1968 the amount of arsenic emitted amounted to about 84 kkg. The peak year for cotton production was 1972 when 13 million bales were produced; in 1974 the amount of cotton was 11.5 million bales, and the average annual production between 1968 and 1974 was 11.2 million bales. Thus, on the basis of cotton production alone, the amount of arsenic emissions from ginning and incineration of cotton trash would not have changed very much between 1968 and the present. However, the portion of cotton upon which arsenicals were used has increased; arsenic acid production has increased by a factor of about 5 on the same interval, but its use is restricted to the Texas-Oklahoma area where the type of cotton grown (accounting for about 40 percent of total production)(113) requires desiccation prior to harvesting. A reasonable factor of increase of overall arsenic use in cotton production would be 2, and assuming no increase in emissions control from cotton ginning and trash incineration, the amount of arsenic emitted to local populations living near ginning facilities would be about twice the figures established in the National Inventory for 1968. (Methanearsonates are used as selective herbicides throughout a large portion of the entire cotton industry, and cacodylic acid is the defoliant most widely used as a cotton harvest and in states other than Texas and Oklahoma.)

There are approximately 3000 ginning facilities distributed throughout the southern and eastern states. The largest number of bales processed at any one facility is about 10,000, corresponding to a potential local emission (based on twice the emission factor given in the National Inventory) of 32 kg. Emissions due to the incineration of gin trash (again, based on twice the National Inventory emission factor of 17 lb As/1000 bales ginned) would be, for a 10,000-bale facility, 155 kg, assuming no emission controls.

With regard to emissions due to other arsenical pesticides, the total amount of pesticides used annually has not changed very much and the National Inventory figure of total emissions of about 3 Kkg would still apply.

Coal

The National Inventory gives the average arsenic content of American coal as 5.44 ppm - ranging from a high for eastern coal of 9.95 ppm to a low of 1.18 ppm for coal from the western states. Approximately 450 million metric tons of coal per year have been consumed,(18) implying that 2,450 metric tons per year of arsenic are associated with this coal.

During combustion, part of the arsenic is released with fly ash and part of it stays with the bottom ash. Measurements of arsenic in stack gases from coal-fired power plants (after fly ash collection) give a range of concentrations of

0.021 mg/m^3 to 0.3640 mg/m^3 (volumes measured at standard temperature and pressure), with an effective value of about 0.1456 mg/m^3. Assuming (after the National Inventory) that 9.97 m^3 of flue gas are generated by each kilogram of coal consumed, the arsenic emissions are about 650 metric tons per year. This is slightly more than one-quarter of the arsenic calculated above to be in the coal.

In an English study cited by Vallee, et al., air measurements of arsenic were made and ranged from 0.03 to 0.105 µg/m^3. It was estimated that the "standard man" exposed to such concentrations would inhale about 0.5 mg/yr. Vallee, et al., also point out that in studies of dust taken from inside of buildings in towns where large amounts of coal are consumed, the "content of copper, lead and zinc in these dusts was much greater than that of arsenic (50 to 400 ppm) and correlates to the content of these metals in coal."(27)

Nonferrous Smelting

Arsenic is produced as a by-product of nonferrous smelting. But it is, for most smelters, considered an impurity which presents a disposal problem. At the present time, there is no economic incentive for most smelters to remove arsenic from their flue gases. In areas such as Arizona where copper is produced and the arsenic content of the ore is relatively low, virtually no effort is made to control emissions. But in areas where high-arsenic ores are smelted, as in the Pacific Northwest States, controls have been required, and Federal Legislation has been directed at making such controls even more stringent.

Atmospheric emissions from nonferrous metals smelting is a local problem, confined generally to distances of no more than 10 to 15 miles of the approximately 40 nonferrous smelting and refining facilities processing the ores of copper, lead, zinc, and gold. All of these ores, especially those mined in the Pacific Northwest, contain arsenic, and unless adequately controlled, arsenic trioxide fumes from smelting facilities enter the air and settle gradually to earth, finding their way onto local grazing and crop lands and onto animals and crops, thus setting the stage for later ingestion in food. And to the extent that such arsenic fumes and dusts are washed into or otherwise moved into water supplies, local - and to some extent even distant - water can come to carry toxicologically significant amounts of arsenic.(115)

Dusts collected from buildings located near smelters have been shown to contain significant amounts (hundreds of ppm) of arsenic trioxide. To the extent such dust can be inhaled or otherwise inadvertantly ingested, it presents a potential hazard.

Tacoma, Washington, and the Helena Valley in Montana are two areas where researchers contend that a public health threat exists due to nonferrous smelting. Nonferrous smelting, of course, takes place in other parts of the country as well, but these two regions have the disadvantage of being close to population centers, and they process high-arsenic-content ores. In a report of a government sponsored study of the Helena Valley,(115) it is stated that arsenic, cadmium, and lead, "which are emitted as air pollutants from (the two plants in the region), settle and accumulate in soil and on vegetation to an extent surpassing levels that are toxic to grazing farm animals. Furthermore, evidence indicates that subclinical effects could be occurring in humans". The study points out that though the average soil content of arsenic is normally about 5 ppm, and the upper 4-inch layer of soil outside the Valley has a geometric mean arsenic content of 6 ppm, the concentration in the upper 4-inch layer within a mile of the smelter complex averages 50 ppm, and sometimes measures up to 150 ppm.

The Tacoma, Washington area is by far the more controversial of the two, especially since it contains the only arsenic refining facility in the nation. A spokesman for the facility at Tacoma has conceded that arsenic exposure has been associated with lung cancer among smelter workers, but that the atmospheric concentrations in the areas adjacent to the facility are "hundreds and even thousands of times" less than in the actual smelting complex. Researchers with that State's Department of Health have, however, found that children who go to school near the plant excrete arsenic in their urine "at about the same level as the workers at the smelter".(112)

Table 17 is a summary of ambient atmospheric concentrations of arsenic for various urban and rural environments. Seven of the 13 measurements listed

TABLE 17

SUMMARY OF AVAILABLE AMBIENT DATA FOR ARSENIC(19)

Site Description	Year(s)	Monitoring Agency	Concentration ($\mu g/m^3$)	No. of Observations	Averaging Time	Analytical Method
Nationwide (urban and nonurban)	1964-65	NASN	0.02	Average of yearly averages for 154 locations	Quarterly Composite of 24-year values	Emission Spectroscopy
Urban, rural, source orientated	Through April 1974	State Agencies of Montana, Washington, Arizona, Colorado	0.13	Average of max. 24-hr observations for 97 sites, 53 locations	24-hour observations	Emission Spectroscopy Atomic Absorption, Arsine Colorimetric
Specific measurements from EPA Data Bank of unusually high concentration						
Tacoma, Wash.						
Center City (70 ft. high sampler)	1965	Washington State Dept. of Ecology	1.3	89	Maximum 24-hour value observed	Emission Spectroscopy
Near ASARCO Copper smelter	1973 (Jan. to Mar.)	Puget Sound Control Agency	4.16 15.9	NA	3 month average of 24-hr concentrations (selected filters) maximum value recorded (24-hr)	
Near ASARCO Copper smelter	1973 (Aug. to Oct.)	Puget Sound Control Agency	1.16 3.9	28	3 month average of 24-hr concentrations (selected filters) maximum value recorded (24-hour)	Atomic Absorption
Near ASARCO Copper smelter	1974 (Jul. to Aug.)	Univ. of Wash.	2.3 5.3	40 NA	Average of 24-hour concentrations Maximum 24-hour value observed	Atomic Absorption
Ajo, Arizona Suburban/Industrial (3 ft. high sampler)	1972	Arizona State Department of Health	4.17	18	Maximum 24-hour value observed	Arsine Colorimetric
Anaconda, Montana						
Center City (26 ft. high sampler)	1962	Montana State Board of Health	2.5	23	Maximum 24-hour value observed	Emission Spectroscopy
El Paso, Tx.	1964	NASN	1.4	NA	Maximum quarterly composite	Emission Spectroscopy
Nat'l Study of U.S. Cities	1953	Litton Summary	0.033	NA	Annual average of 24-hr samples (composite of 16 cities)	NA

exceed the proposed standard of 2 $\mu g/m^3$ averaged over an 8-hour period. Two of the measurements at Tacoma, Washington, have average 24-hour concentrations that exceed the proposed standard.

In the nonferrous-metals portion of this study it is shown that the total volume of arsenic in the ore concentrates of zinc, lead, and copper are:

zinc	525 kkg/yr
lead	1,060 kkg/yr
copper	35,000 kkg/yr

Thus, copper concentrate carries the largest portion of arsenic in the nonferrous metals industry; also, based on the Bureau of Mines production statistics for 1973, the amount of arsenic per metric ton of copper produced is significantly higher than for lead and zinc.

zinc	(1.36×10^6 kkg in 1973)	0.385 kg As/kkg Zn
lead	(1.36×10^6 kkg in 1973)	0.78 kg As/kkg Pb
copper	(2.2×10^6 kkg in 1973)	15.9 kg As/kkg Cu

The amount of this arsenic that is released to the air as a result of smelting operations is about 5230 kkg, which is only about 14 percent of the total arsenic in the ore concentrates, but the largest portion is from the copper industry - 2.2 kg As per kkg of copper produced, versus 0.176 kg/kkg for lead and 0.140 kg/kkg for zinc. Of this total annual atmospheric arsenic emission, 92 percent is due to copper smelting.

Arsenic in Water

Arsenic enters natural water systems from these sources:

1. Natural sources:
   - (a) Natural erosion processes including microbially-mediated erosion.(5)
   - (b) Geothermal processes which may lead to very high arsenic levels in locales where hot springs carry arsenic to the surface.(5,22)

2. Artificial sources:

   (a) Pesticide runoff
   (b) Smelter fallout
   (c) Erosion processes stimulated by mining and excavation operations
   (d) Runoff of agricultural fertilizers containing arsenic as an impurity
   (e) Deep-well drilling, especially geothermal areas where nonferrous sulfides reside; the heated water mobilizes arsenic to the surface.
   (Bores drilled for geothermal power in New Zealand delivered 190,000 kg of arsenic in the year 1964.(22)

Mobile arsenic becomes either locked into highly insoluble soil (or sediment) complexes where it is effectively removed as an environmental hazard, or it moves from the air and from soil into the water resources which carry it to the oceans. While in fresh natural waters, arsenic poses a potential health hazard to those who drink the water and to those who eat food that has been grown in or near such waters. Water-borne arsenic is probably the main source of ingested arsenic for the general population - as opposed to local populations exposed to industrial operations.

Chronic arsenic poisoning has been reported associated with drinking water containing concentrations of arsenic ranging from 0.21 to 10.0 mg/l. Concentrations of 0.05 to 0.25 mg/l have also been reported as having no ill effect. The current standard for drinking water in the United States (established by the Public Health Service in 1962) is 0.01 mg/l, recommended maximum concentration, and 0.05 mg/l, the maximum permissible concentration. A 1969 survey of 969 drinking water supplies in the U.S. found arsenic exceeding 0.01 mg/l in 0.5 percent of the samples, and exceeding 0.05 mg/l in 0.2 percent. Ferguson and Gavis, in reporting these figures, feel that these concentrations indicate no current threat to the public health.(5)

In two surveys of fresh surface waters in the U.S. in 1970 and 1971, the arsenic concentration exceeded the 0.01 mg/l level in about 7 percent of 1500 samples from 150 rivers and in 21 percent of 727 samples from rivers and lakes. The mean arsenic concentration of the samples exceeding the 0.01 mg/l limit in the first survey was 0.1 mg/l, which is ten times the U.S.P.H.S. recommended maximum concentration and 2 times greater than the permissible limit.(5)

The hazard of arsenic in water is a function of the chemical state of the arsenic, trivalent versus pentavalent. The reduced, or trivalent inorganic arsenite form is the most hazardous, 10 to 60 times more toxic than arsenate. Arsenic compounds in water, whether they are organic or inorganic, tend to oxidize to inorganic arsenates; but the chemical equilibrium relationship between +3 As and +5 As in natural waters has not been adequately determined. It is generally agreed that arsenates exceed arsenites in oxidizing aquatic environments, but the oxidation to arsenate rarely proceeds to completion. In one study of ocean waters, the ratio of +5 As to total As was close to 0.8. However, in lakes and rivers where residence times are short, Ferguson and Gavis state that unless the oxidation is catalyzed by microorganisms, oxidation "cannot advance very far".(5)

The minimum concentration of arsenic in drinking water for which a toxic effect (chronic) has been noted is 0.21 mg/l.(5) This is only 4 times greater than the maximum permissible concentration established by the PHS. If, however, this level of 0.21 mg/l was largely of the reduced arsenite form, then the factor of safety between the maximum permissible concentration and the approximate threshold level of intoxication due to arsenate would be between 40 and 240, certainly a comfortable margin for any eventuality of chronic arsenic ingestion from air to food. However, the ratio of arsenite to arsenate in drinking water and in fresh surface waters has not been measured to any significant extent. Braman and Foreback measured the amounts of arsenate and arsenite in fresh waters in Florida.(28)

	+3 As (ppb)	+5 As
Hillsborough River	<0.02	0.25
Withlacoochee River	<0.02	0.16
Well water near Withlacoochee River	<0.02	0.27

	+3 As	(ppb)	+5 As
Remote pond, Withlacoochee Forest	<0.02		0.32
Univ. Research Pond, Univ. of S. Fla.	0.79		0.96
Lake Echols, Tampa	2.74		0.41
Lake Magdalene, Tampa	0.89		0.49

For these few samples, the ratio of arsenite to arsenate is near to zero for the first three samples, and it varies from close to 1 up to nearly 7 in the remainder. More information of this type is needed, and its relationship to human activity and to the environmental circumstances of the bodies of water.

With regard to food - from both animal and plant sources - grown in arsenic contaminated waters, studies indicate that while bioaccumulation of arsenic does take place to a very high degree(5,22,27,28,116) (measured as high as 71,000 times the ambient concentration for dried seaweed),(116) the arsenic that accumulates in both plants and animals is of a form that presents virtually no hazard upon ingestion.(5,27,116) Woolson cites a study in which shrimp containing 128 ppm As were fed to rats at a dietary level of 13.3 ppm; they were also fed As_2O_3 at the same level.(116) The rats' livers contained 20-fold less arsenic with the shrimp diet, and more than 98 percent of the arsenic fed in the shrimp was excreted within 4 days. Humans fed shrimp excreted all the arsenic within 4 days.(5,116)

The technology currently exists for the monitoring of arsenic (both organic and inorganic and in its tri- and pentavalent states) in fresh and salt waters and in all aquatic organisms; lower limits of detection of 1 ng are possible.(5,28) Surprisingly little work has been done, however, in measuring the relative portions of arsenic compounds and valence states in water and in aquatic organisms. To the extent that research has been carried out, though, the main hazard of arsenic in water is evidently not through the eating of organisms from aquatic waters (except possibly in cases of extreme arsenic pollution), but rather derives from the drinking of water containing inorganic trivalent arsenic.

Arsenic in Food

The tissues of plants and animals grown in arsenically-polluted surroundings accumulate arsenic. Table 14 lists the arsenic content of foods as measured by various researchers.

Seafoods contain the highest levels of arsenic found in commonly available foods; this is especially so of seafood harvested in coastal waters located adjacent to outlets of arsenic-contaminated rivers. Many marine organisms, both plant and animal, bioaccumulate arsenic in their bodies hundreds and even thousands and tens of thousands of times above the ambient levels. But there is evidence such arsenic is not retained very long after ingestion of such organisms, and studies to prove biomagnification (increasing tissue levels at higher positions up the food chain) have shown that such does not apparently take place.(5,22,27,116)

Numerous cases of arsenic poisoning due to food contamination have been reported,(27) but all of the reported cases were the result of contamination that took place as a direct result of pesticide residues (apples have been reported to contain 1 to 2 mg lead arsenate) or because of arsenic contamination resulting from food processing (e.g., the use of arsenically contaminated sulfuric acid to modify sugar used in the production of beer resulted in 70 deaths and 6000 illnesses in England in 1900).(27) No evidence was discovered in this study that arsenic taken up by food organisms in natural biological processes has caused a toxic effect, either chronic or acute, though it is conceivable that under extreme conditions marine organisms such as shrimp and certain edible marine plants grown in highly contaminated waters might pose a chronic health threat.

Arsenical feed additives are used in the feed of swine and poultry to increase growth rates and feed efficiency. Federal law requires a 5-day withdrawal period from arsenical feed additives prior to sending the animals to market. Tissue levels of arsenic in poultry and pork reaching the market are well within the Federally established standards.(59)

The incidence of arsenic intoxication due to pesticide residues has been decreasing over the past three decades in relation to the decreasing use of arsenical pesticides and the enforcement of residue standards. The largest area of potential hazard due to arsenic residue on foods in in foods grown near non-ferrous smelting facilities; the State of Washington has warned Tacoma residents who grow vegetables in the region of fallout from the smelter there that there is a potential hazard due to both arsenic and cadmium; but people continue to raise and eat vegetables, with no evidence of arsenical intoxication having yet been reported. Studies of arsenic uptake in vegetable crops$^{(35)}$ have shown that even at soil levels sufficient to cause a 50 percent reduction in plant growth, the uptake of arsenic is not appreciable. (This is discussed below.) The arsenic is such crops is probably of a form which is much less toxic than the trivalent inorganic form. Thus, the chief hazard potential to persons who eat crops grown in the vicinity of smelters is from arsenic which has been deposited on the vegetable surface as a result of fallout.

Arsenic in Soil

As discussed in the section on soil chemistry, the fate of arsenic in soil is a function of soil content of iron, aluminum, and calcium adsorption sites and of soil pH, humus content, and available phosphorus (i.e., phosphorus in solution), which competes with arsenic both for adsorption sites within the soil and for plant uptake. Additionally, the amount of available arsenic varies with time, increasing or decreasing in complex relationship to the other soil variables, but generally reaching chemical equilibrium (i.e., reaching a fairly constant ratio of available-to-total arsenic) within several months after initial application.

Agricultural soils typically contain several ppm of total arsenic. In a study by Woolson,$^{(35)}$ three soil types were used to study phytotoxicity and plant uptake in various crops. The initial total levels (ambient levels) for the soils were:

Soil	Total Arsenic (ppm)
Lakeland (L)	1.2
Hagerstown	4.5
Christiana (C)	3.5

Assuming a "worst-case" condition (i.e., soil from which there is no losses of arsenic via leaching, runoff, volatilization, or any other means) how much arsenic would have to be added, and over what period of time, to double the ambient levels? The answer is based upon these considerations:

1. An acre of agricultural soil, as measured to a depth of a "furrow slice", is taken as weighing 1 million pounds,(38) or about 450 kkg.
2. The six most common arsenical pesticides, their dosage ranges and arsenic are:

	Dosage range (kg/acre)	% As	Effective As dosage
Lead Arsenate	1 - 2.5	22	.22 - .55
Calcium Arsenate	1 - 2.5	38	.38 - .95
Arsenic Acid	2	53	1.06
Cacodylic Acid	1	54	.54
DSMA	2	41	.82
MSMA	1.5	46	.69

Thus, for the three soils listed, the number of dosages of the above compounds sufficient to double the initial (ambient) total arsenic content are:

Ambient (ppm)	1.2	4.5	3.5
Lead Arsenate (doses)	1 - 2.5	3.5 - 9	3 - 7
Calcium Arsenate	.5 - 1.5	2 - 5.3	1.5 - 4
Arsenic Acid	.5	2	1.5
Cacodylic Acid	1	4	3
DSMA	.75	2.5	2
MSMA	.75	3	2.5

Thus, assuming one dose per year for each arsenical, in some cases (e.g., arsenic acid in soil L) half a dose will double the total soil arsenic level, while in others, such as lead arsenate on soil type H, 9 doses (or 9 years) are required.

In the real world, however, soil arsenic levels, both total and available, decrease from initially high levels. And since it is the available (soluble) arsenic which determines plant toxicity and uptake, available arsenic is tabulated below for the three soils for various initial arsenate application amounts as a function of time.(35)

Soil	Arsenate Applied (ppm As)	Available Arsenic After:		
		0 Months	4 Months	9 Months
L	10	1.4	3.0	3.7
	50	20.0	18.0	20.7
	100	48.3	35.0	55.0
	500	384.0	377.0	288.0
H	10	1.0	0.6	<0.1
	50	6.0	4.1	4.0
	100	18.3	5.7	9.8
	500	276.0	126.00	120.0
C	10	2.6	2.1	1.7
	50	18.3	19.3	8.2
	100	52.3	22.0	19.2
	500	429.0	260.0	138.0

The significance of these numbers is apparent in terms of phytotoxicity to the various crops studied by Woolson. For example, the most "arsenic-tolerant" soil is soil H - that is, the six crops tested by Woolson, grew best at any given applied arsenate level in soil H, which, as can be seen above, has the lowest available arsenic levels. Thus, in soil H, at 100 ppm arsenic initially applied, all six crops tested (green beans, lima beans, spinach, cabbage, tomatoes, and radishes) would be able to produce a crop at the 4-month and 9-month levels of available arsenic. (Considering arsenic acid, which has the highest recommended arsenic dosage of the agricultural arsenicals considered here, the number of doses (years) necessary to achieve a total arsenic level of 100 ppm would be about 43 - and again, this assumes no losses of arsenic from the soil by any means, whereas in reality much arsenic would be removed by the natural methods listed in the soil chemistry section of this study; and even if not removed from the soil, the large portion of the applied arsenic would not be available for phytotoxicity or plant uptake in any way, as evidenced in the above table.)

However, other soils, represented here by soil L, are less tolerant of arsenic; phytotoxicity takes place at lower total applied levels. In another study, by Woolson, et al.,(117) soil types L and H were given initial doses of 100 ppm of sodium arsenate, and the available water-soluble arsenic was recorded as a function of time. The available arsenic in soil H dropped to about 10 ppm within 1 week while soil L required more than 24 weeks to decrease to 10 ppm available arsenic.

The L soil, however, because of the longer period required for the available arsenic to become unavailable (i.e., fixed in the soil), has the advantage of being able to more rapidly reduce its total arsenic content; the water-soluble arsenicals are more prone to leaching deeper into the soil or of being carried away with water runoff than are the fixed arsenicals in the H soil where fixation takes place rapidly.

Soil H, because of its rapid soil fixation of arsenic, is more prone to accumulation of arsenic if the annual doses are of a sufficiently high volume. That is, the soil cannot continue to fix arsenic indefinitely - each year the rate of fixation would tend to decrease if the amount of applied arsenic exceeds the amount that can be annually removed by the various natural processes. Research as to a threshold value for such an annual dosage volume has not been uncovered in this study, probably because it does not exist. However, since in any real soil upon which arsenicals have been used the ratio of available-to-total arsenic is always greater than zero (the actual chemical equilibrium values of available-to-total soil arsenic are a function of soil type), total soil arsenic will always tend to decrease toward the ambient level, which is the level corresponding to the natural movement of arsenic into and through the soil.

In Woolson's study of six crops,(35) the amounts of available arsenic necessary to cause a 50 percent growth reduction (GR_{50}) were:

	GR_{50} (ppm)
Green Bean	6.2
Lima Bean	10.9
Spinach	10.6
Cabbage	48.3
Tomato	25.4
Radish	19.0

The concentration of arsenic in the dried edible portions of these crops at the GR_{50} level of available soil arsenic were:

	Dried edible portion (ppm)
Green Bean	4.2
Lima Bean	1.0
Spinach	10.0
Cabbage	1.5
Tomato	0.7
Radish	76.0

The GR_{50} level is effectively the economic limit at which a crop can be grown; greater growth reduction will not result in a marketable crop.

Comparing the available soil arsenic to the plant arsenic (edible portion) at GR_{50} (above two tables), it is evident that, except for the radish, bioaccumulation does not take place as happens with freshwater and marine plants. Bioaccumulation ratios (BR, ratio of water concentration to plant concentration of a material) for fresh water plants range from 3 to 20,000 and for marine plants, from 50 to 70,000. Of course, for plants grown in soil, the concentration of available arsenic is based upon the soil itself rather than upon the water in the soil, for which the bioaccumulation ratio would undoubtedly be higher, but not as high as for aquatic plants.

The identity of the arsenic compound or compounds in land-grown crops is not known. However, studies of aquatic plants have shown it to be present as both water- and lipid-soluble arseno-organic compounds. Woolson, referring to Lancaster, et al., points out that lake weeds containing 288 ppm arsenic were fed to sheep as 20 percent of the total diet for 3 weeks with no ill effects on the animals' health. Tissue residues of arsenic did increase during the period, but decreased when the weed was removed from the diet.(116)

In the case of the 76-ppm radishes, assuming that radishes normally contain 93 percent water,(23) the arsenic concentration would be on the order of 5.3 ppm in a corresponding fresh, undried radish. Assuming further (worst case) that the arsenic in such radishes is of a form having a toxicity equivalent to trivalent inorganic arsenic and that the arsenic would be completely absorbed from the alimentary canal upon ingestion, then the amount of radishes required to produce a minimal toxic effect - on the order of 10 mg arsenic - would be about 150 3-cm-diameter radishes. It is likely the symptoms of arsenic toxicity, even in this worst-case situation, would be masked by those of ordinary overindulgence.

With regard to plant uptake of soil arsenic, Vallee, et al. observe that "soil concentrations of arsenic may rise to many hundred parts per million after years of spraying with lead arsenate and other pesticides", and "experimental attempts to sterilize fresh soil have sometimes required huge amounts of arsenical compounds". Nevertheless, small amounts of arsenic may be taken up by plants grown in heavily contaminated soil, "but rarely in quantities sufficient to constitute a human risk".(27)

SECTION VIII

THE MARKET FOR ARSENIC

Domestic Arsenic Supply

All of the domestic arsenic production is in the form of white arsenic, As_2O_3, and is derived from collected flue dusts from copper smelting. Moreover, the entire U.S. production since 1959 has been at one location - the Tacoma, Washington plant of ASARCO. Up until 1959, white arsenic was produced at two other plants, the Anaconda Co. plant at Anaconda, Montana, and the U.S. Smelting, Refining, and Mining Co. plant at Midvale, Utah.$^{(141)}$

Because there is a single producer of white arsenic in the U.S., recent production data has not been released by the Bureau of Mines. However, Table 18 lists these data up until 1968 as reported by the Bureau of Mines. In addition, Table 18 also lists the price history for white arsenic, and the production of primary refined copper from domestic ores. The price for white arsenic is listed in terms of constant 1974 dollars; up until 1968, the correction for inflation was based upon Bureau of Mines data,$^{(17)}$ and later corrections were based upon the Bureau of Labor Statistics wholesale price index for intermediate industrial materials.$^{(142)}$

The U.S. production of white arsenic in any year is dependent upon the quantity of copper ore smelted, and upon the world price for white arsenic. The data of Table 18 from 1949 through 1968 (20 years) were analyzed to quantify this dependence. The results were a regression equation:

$$Y_c = 5{,}160 + 3{,}300\left(\frac{X_1 - 227}{150}\right) + 2{,}310\left(\frac{X_2 - 947{,}000}{500{,}000}\right)$$

where Y_c = Calculated U.S. Production of White Arsenic, Metric Tons Per Year
X_1 = White Arsenic Price, Constant 1974 Dollars Per Metric Ton
X_2 = U.S. Production of Refined Primary Copper from Domestic Ore, Metric Tons Per Year

TABLE 18

SUPPLY STATISTICS FOR ARSENIC TRIOXIDE
SOURCES: BUREAU OF MINES(17,18,70,141), JILER(143)

Year	U.S. As_2O_3 Production, kkg/year	Price, Actual Dollars per kkg As_2O_3	Price, Constant 1974 Dollars per kkg As_2O_3	U.S. Cu Production from Domestic Ores, kkg/year	U.S. Imports of As_2O_3, kkg/year	U.S. Consumption of As_2O_3, kkg/year	World Production of As_2O_3, kkg/year
1949	5,580	117	271	630,000	8,300	13,900	
1950	5,790	132	310	835,000	24,100[b]	29,900	
1951	7,400	139	314	864,000	19,400[b]	26,800	
1952	6,820	132	279	837,000	6,000[b]	12,800	
1953	4,830	123	258	845,000	9,800[b]	14,600	
1954	5,760	123	253	764,000	9,400[b]	15,200	
1955	4,740	123	250	904,000	12,900[b]	17,600	
1956	5,480	123	243	979,000	17,800[b]	23,300	
1957	4,570	123	235	952,000	16,600[b]	21,200	
1958	5,060	123	232	910,000	13,700[b]	18,800	
1959	2,340	101	183	723,000	22,100[b]	24,400	
1960	6,000	104	183	1,018,000	16,100[b]	22,100	
1961	5,100	93	157	1,071,000	17,600	24,600	53,500
1962	5,400	93	157	1,102,000	14,300	24,400	45,000
1963	4,900	116	196	1,104,000	13,200	25,300	48,400
1964	4,500	118	199	1,142,000	16,500	29,400	52,700
1965	7,000	126	212	1,211,000	14,100	28,900	51,000
1966	5,500	118	199	1,227,000	16,900	28,600	52,000
1967	2,900	126	204	769,000	24,500	31,300	58,800
1968	3,500	133	206	1,053,000	22,800	28,800	61,200
1969	6,700[a]	143	216	1,331,000	16,500	23,200[c]	49,800
1970	6,700[a]	143	208	1,380,000	17,000	23,700[c]	49,500
1971	6,100[a]	143	200	1,280,000	15,700	21,800[c]	50,300
1972	7,000[a]	143	190	1,523,000	12,300	19,300[c]	45,400
1973	6,900[a]	143	178	1,557,000	10,400	17,300[c]	47,400
1974	8,700[a]	286	286	1,440,000	13,600	22,300[c]	47,600

[a] Estimated by Regression Analysis of Prior Years

[b] Estimated from Consumption and Production Data

[c] Estimated from Production and Imports Data

Figure 1 compares Y_c, the calculated domestic As_2O_3 production level, with the reported production data of Table 15. The standard error in Y_c is 960 metric tons per year.

The influence coefficients in the regression equation indicate (as they should) that the U.S. production of white arsenic increases as both the price and the copper production increase. The two coefficients (of the two normalized variables) are of comparable magnitude, implying that both variables are of similar importance.

The regression equation was then used to calculate domestic As_2O_3 production data for the years 1969 through 1974. The calculated 1974 level, 8,700 kkg of As_2O_3 (equivalent to 6,550 kkg of arsenic) is lower than other values independently estimated elsewhere in this report (8,180; 8,300; and 12,250 kkg of arsenic). As an upper limit, the plant capacity of ASARCO/Tacoma was reported as 33 metric tons of As_2O_3 per day, or 12,000 metric tons of As_2O_3 per year on a 365-day basis.(69c)

Figure 2 shows supply curves for domestic white arsenic, at several levels of domestic copper production, derived from the regression equation for As_2O_3 production. If the market price is less than $50 per metric ton, it is likely that domestic production will cease; e.g., it will no longer pay to refine and sell the white arsenic. Although the 1974 level of primary copper production from domestic ores was about 1.5 million metric tons per year (at a price of $1.70/kg), the Bureau of Mines projected that the copper production would reach 2.275 million kkg at $2.57 per kg (in constant 1974 dollars).(17)

There are many important and new factors affecting domestic white arsenic production which the historical data (and so the regression equation and Figure 2) do not take into account:

1. The past few years have witnessed a rapid increase in the quantities of copper ore which are leached. In 1968, 12 percent of the total domestic mine production was cement copper;(17) this had grown to 15 percent by 1972.(70) Since much less arsenic accompanies cement copper from the mine than copper ore concentrates from the mine, the

FIGURE 1

CALCULATED VS. REPORTED
U.S. PRODUCTION OF WHITE ARSENIC
1949-1968

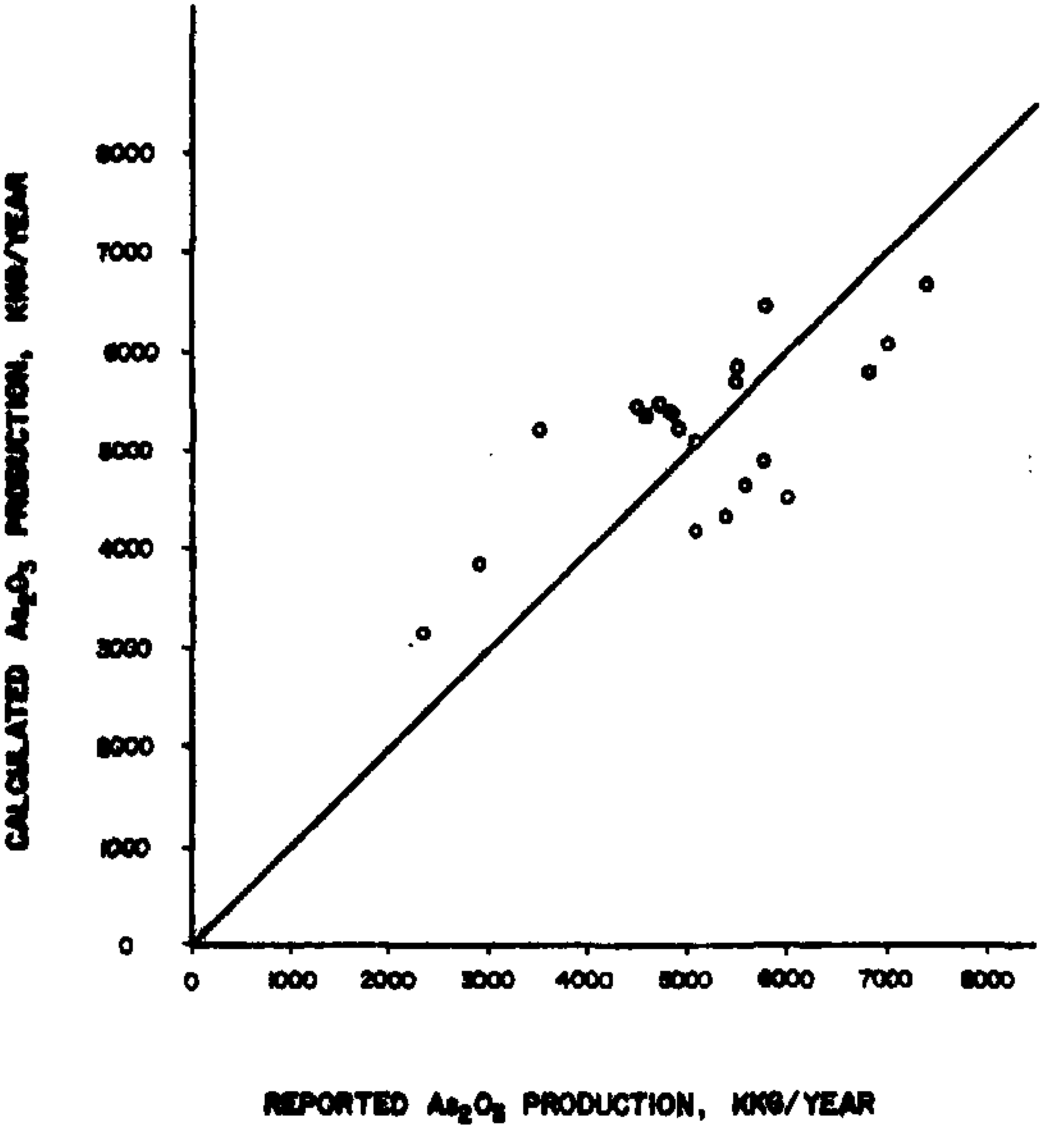
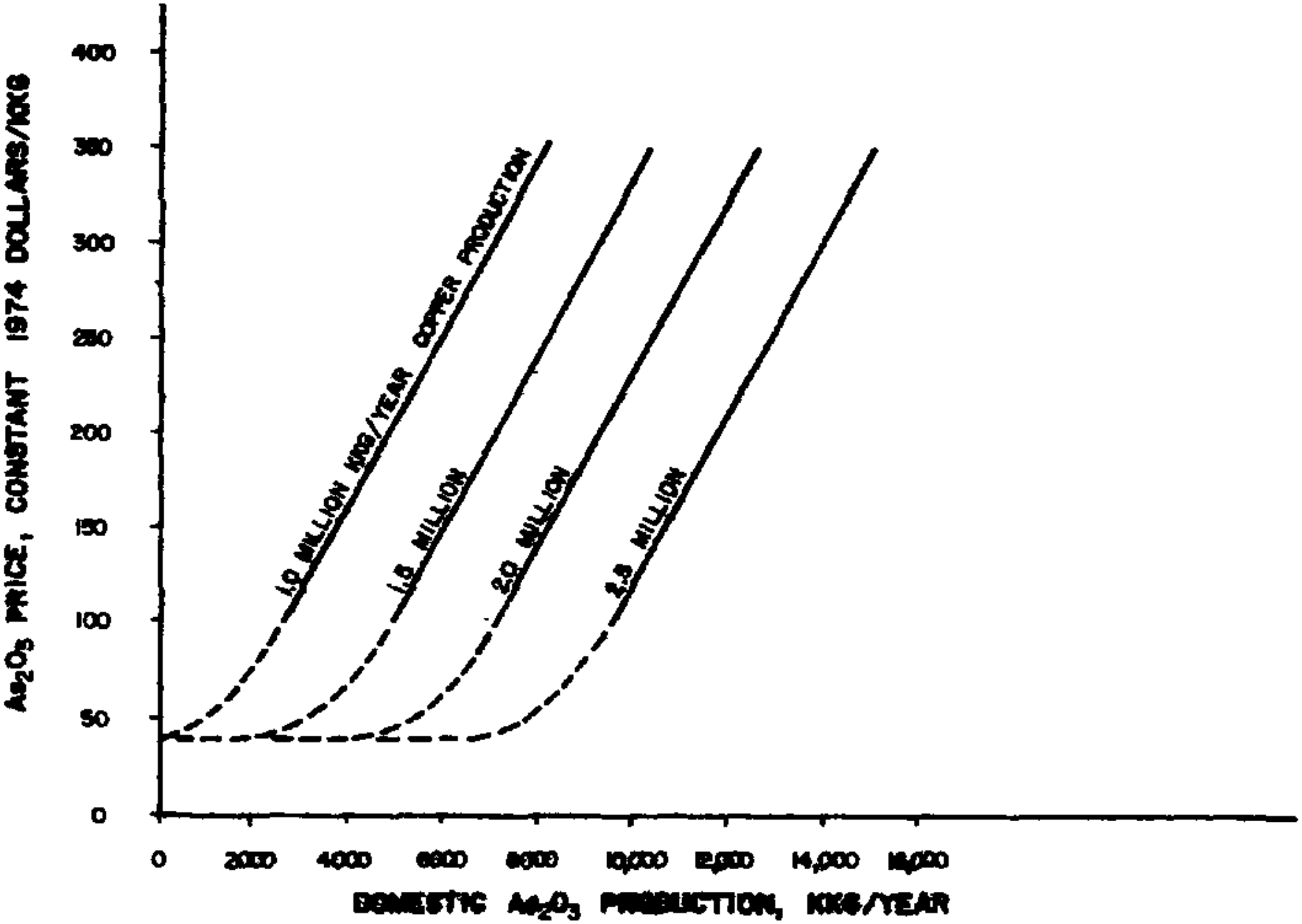


FIGURE 2

DOMESTIC PRODUCTION OF WHITE ARSENIC



ratio of total available arsenic to copper product should be decreasing. On the other hand, since the recovered As_2O_3 is such a small fraction of the total available arsenic, the impact of leaching may not be significant with respect to the domestic supply of As_2O_3.

2. The past few years have also witnessed a marked improvement in controlling sulfur dioxide emissions from copper smelters. Previously, relatively few smelters had acid plants (for reasons stated earlier in this report). The impact of environmental forces upon the industry has been to extend SO_2 control (and subsequent acid production) to a target of 90 percent capture. With greatly increased emission control, the particulates (which include As_2O_3) formerly released to the atmosphere are now being captured to a greater degree. Hence, gas cleaning processes upstream of acid plants should be recovering much greater quantities of arsenic. The portion recovered via dry dust collection (electrostatic precipitators and baghouses) should increase the commercial supply of arsenic, while the portion removed via wet scrubbing should not. It also appears that the enforced recovery of more SO_2 has played a part in the increase in copper ore leaching, by providing a source of sulfuric acid.

3. The recently-proposed arsenic standards by the Occupational Safety and Health Administration, if promulgated, could drastically affect the commercial supply of arsenic in either direction. Enforced recovery of arsenic to meet tighter ambient standards could increase the supply. However, the tighter standards may conceivably shut down the sole producer of white arsenic, if ambient standards in the As_2O_3 plant are too expensive to meet.

4. The discussion of the commercial occurrence of arsenic (elsewhere in this report) revealed that potential sources for arsenic other than copper ores amount to twice the copper-related resource. Much of these potential (but unexploited) sources are not technically or economically practical under any reasonable set of market circumstances, either because the arsenic is at extremely small concentrations or because the arsenic is tightly bound. However, there remain relatively large and feasible untapped resources for arsenic (should there ever be sufficient demand for arsenic). Among these feasible resources are phosphoric acid (555 kkg/year) and Searles Lake brines (2,160 kkg/year). Feasible arsenic resources which should become very sizable in the next few decades are associated with coal gasification and with geothermal energy.

For the above reasons, the domestic supply of arsenic may conceivably increase by dramatic proportions in the next few years, or may conceivably be reduced to zero. The conclusion is therefore reached that no long-term (i.e., ten years) projection may be made with any meaningful certainty.

World Arsenic Supply and Total U.S. Supply

Table 18 also lists the world production of white arsenic from 1961 through 1974. For those years, the U.S. production amounted to about 10 percent of the world production. The world production data is shown in Figure 3. It is apparent that the quantity of white arsenic produced is not strongly correlated to price. Hence, the world supply curve of Figure 3 was drawn vertically (e.g., completely inelastic supply) in the range of the historical data ($150 to $300 per metric ton).

At the lower range of Figure 3, the world supply curve was drawn with increasing supply elasticity; marginal refiners will drop out of the marketplace as the price approaches $50 per metric ton. Above $300 per metric ton, those with crude arsenic resources (either as a waste material or as a byproduct) will be

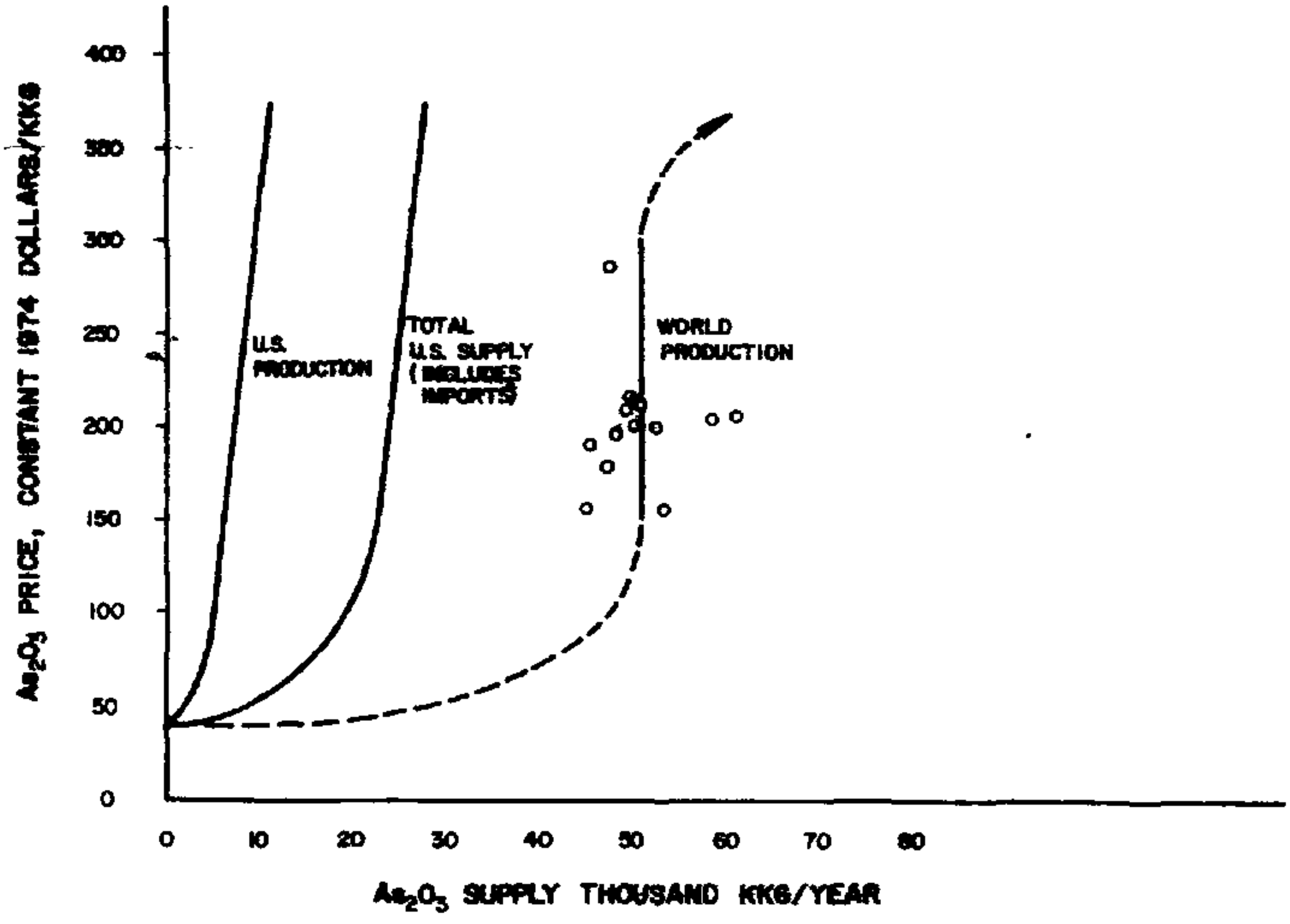


FIGURE 3

WORLD SUPPLY OF WHITE ARSENIC

induced to refine and market these resources. It has been shown that non-copper resources of arsenic are potentially large, and that unrecovered copper resources of arsenic are also large. Hence, it is implied by the arrow at the upper end of Figure 3 that an entirely different supply regime for arsenic exists but has yet to be quantified.

The present world supply is not totally related to copper ore, as it is in the United States. As the data in Table 19 indicate, several countries important in arsenic production are not important in copper production, and visa versa.

Also shown in Figure 3 is a curve for the total 1974 U.S. supply (domestic production plus imports) of white arsenic. This latter curve was constructed as parallel to the domestic production curve of Figure 2 (at a copper production rate of 1.5 million metric tons per year).

Demand for Arsenical Insecticides

Prior to 1952, very large quantities of arsenical insecticides were consumed:

Insecticide	Composition	As_2O_3 Content	Applications
Paris Green	$Cu(OOCCH_3)_2 \cdot 3\ Cu(AsO_2)_2$	55%	Potatoes, Mosquitos
Lead Arsenate	$PbHAsO_4$	32%	Potatoes, Apples
Calcium Arsenate	$Ca_3(AsO_4)_2 + CaO$	50%	Cotton, Apples

In 1940, the consumption of lead arsenate and calcium arsenate were (respectively) 34,100 and 22,700 metric tons,(48) equivalent to a total of 22,300 metric tons of white arsenic. The demand dropped drastically from 1940 to 1949; in the latter year, the U.S. demand for <u>all</u> uses of As_2O_3 was only 13,900 metric tons. Higher cotton prices and increased cotton planting in 1950-1951 temporarily increased the demand for calcium arsenate for boll weevil control; the total U.S. demand for As_2O_3 in the 1950's was dependent from year-to-year upon the degree of boll weevil infestation.

TABLE 19

PRODUCTION OF ARSENIC AND COPPER BY COUNTRY IN 1972

SOURCE: BUREAU OF MINES(70), JILER(143)

Country	As_2O_3 Production, Metric Tons/Year	Copper Production Metric Tons/Year
United States	7,000	1,510,000
France	10,000	500
U.S.S.R.	7,200	664,000
Mexico	591	78,600
Sweden	16,000	24,700
Peru	1,020	225,000
W. Germany	500	1,320
Japan	427	113,500
S.W. Africa	4,000	32,400
Brazil	164	4,300
Portugal	190	4,800
Canada	27	725,000
Spain	-	32,100
Chile	-	724,000
South Africa	-	162,000
Zaire	-	429,000
Zambia	-	716,000
Phillipines	-	205,000
Australia	-	185,000
World	45,400	6,630,000

In the 1960's, the arsenical insecticides received strong competition from organic insecticides, so that by 1971 only 1.4 percent of all insecticides used on crops were arsenicals; and the quantity of arsenical insecticides used on crops amounted to only 1,260 metric tons (90 percent of which was used on apples and other fruits - virtually none was used on cotton or potatoes).(49) However, non-crop consumption of arsenical insecticides amounted to more than an equal quantity, and were typically used by homeowners. From 1965 through 1972, the average consumption both for crops and for other uses was:

	Insecticide Consumption, Metric Tons/Year	Equivalent As_2O_3, Metric Tons/Year
Lead Arsenate	3,500	1,100
Calcium Arsenate	900	450
Paris Green	7,300	4,000

Hence, the equivalent As_2O_3 demand during this period, for insecticides, amount to 5,550 metric tons per year. The wholesale prices during the 1970 to 1972 period were relatively stable at about $800 per metric ton for lead arsenate and about $410 per metric ton for calcium arsenate (about $1,100 and $550, respectively, in constant 1974 dollars).(144) The higher price of the lead arsenate reflects, of course, the high cost of lead oxide or lead nitrate.

Both lead and calcium arsenates are manufactured from arsenic acid, which in turn is made from white arsenic. In 1970-1972, the prices for arsenic acid (100 percent basis) and for white arsenic were respectively (in constant 1974 dollars) about $750 and $200 per metric ton. An analysis of ingredient costs is:

Product	Ingredient	kkg Ingredient / kkg Product	Cost of Ingredient Per kkg Product	Product Price, $/kkg
Arsenic Acid	White Arsenic	0.70	$140	$ 750
Lead Arsenate	Arsenic Acid	0.46	$345	$1,100
Calcium Arsenate	Arsenic Acid	0.50	$375	$ 550
Paris Green	White Arsenic	0.55	$110	$ 400

It is apparent that the arsenic-bearing starting material is an important factor in determining the price of lead arsenate and paris green, and is the critical factor in determining the price of calcium arsenate. The demand for arsenical insecticides has been decreasing recently because of competition from organic insecticides, because of the cancellation of crop registrations, and because of tighter OSHA constraints upon the manufacture of arsenicals. The 1975 price for lead arsenate is about $600 per metric ton, much less than in the 1970-1972 period,(145) despite the increased cost of the arsenic-bearing ingredients, and despite the increased price of the organic insecticides which compete for its use.

Based upon the above discussion, the As_2O_3 demand curve for insecticides was constructed as shown in Figure 4. This curve passes through the 1970-72 point of 5,550 kkg/year at a price of $200 per metric ton of As_2O_3. The curve was drawn to be relatively inelastic from $100 to $400 per metric ton on the rationale that the use of arsenical insecticides is already a small fraction of the total insecticide demand; so that its use is highly selective and not likely to change drastically with price. At higher As_2O_3 prices, the curve reflects greater demand elasticity, as alternate (i.e., organic) insecticides may be substituted for arsenicals. At lower As_2O_3 prices, some increase in demand is shown, but it is not anticipated that arsenicals would make major inroads on the total insecticide market.

Demand for Arsenical Desiccants and Defoliants

Arsenic acid use for the desiccation of cotton has rapidly increased since the mid-1960's:(49,53,146,147)

Year	Arsenic Acid Used, kkg/year (100% Basis)	Equivalent As_2O_3, kkg/year	Arsenic Acid Price, 1974 $/kkg
1968	965	724	$ 620
1969	1,290	969	650
1970	1,620	1,212	690
1971	1,950	1,460	740
1972	2,760	2,070	760
1973	3,600	2,700	760
1974	4,400	3,300	780
1975	(5,600)	(3,920)	(880)

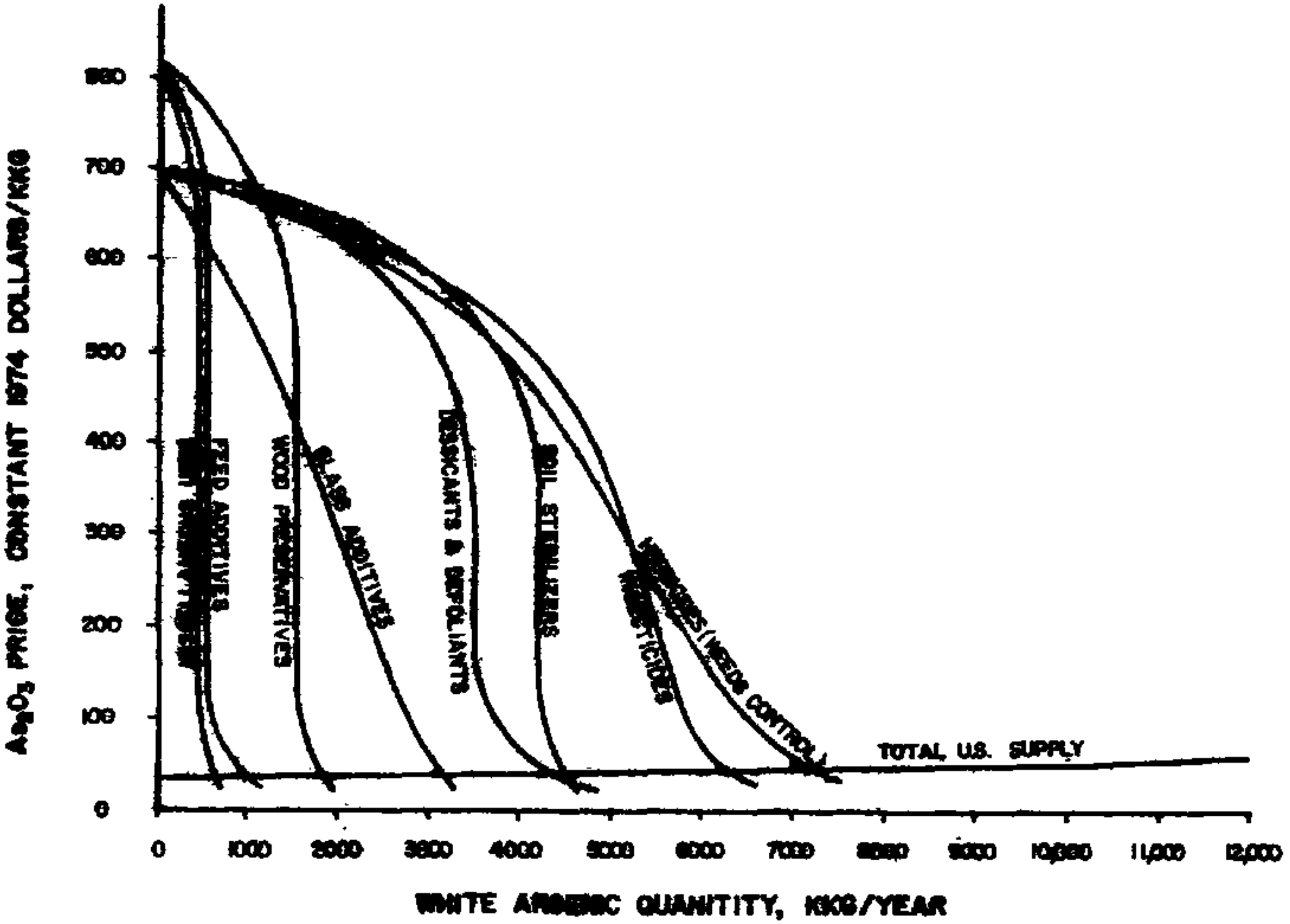


FIGURE 4

DOMESTIC MARKET FOR WHITE ARSENIC

The use of arsenic acid to terminate the cotton plant is considered mandatory in the Blackland area of Texas.(148,149) The convincing arguments include:

1. Early maturity and harvest followed by early stalk destruction is an integral part of the pest management program. Desiccation removes the available food supply for boll weevils. Arsenic acid is the only desiccant that constantly terminates the cotton plant, especially in higher rainfall areas, and arsenic acid is the only effective compound for controlling re-growth.
2. Arsenic acid renders plant parts brittle for mechanical stripping of the bolls. Mechanical spindle picking is too expensive, and waiting for frost would incur heavy insect losses. A self-propelled stripper costs approximately $20,000; a spindle picker costs twice as much. A stripper can harvest as much as 70 bales per day, while a mechanical picker can only harvest 20 bales per day in good-yielding cotton. Pickers are more useful in high yield areas (2 bales per acre or more).
3. Without effective desiccation, stripping results in large quantities of "green trash" which cause major problems at the cotton gin. In addition to stoppages ("choke-ups"), heating would decrease lint and seed quality.

Cacodylic acid is also used as a cotton harvest aid, in the cotton states other than Texas and Oklahoma. Its use as a defoliant is new, dating back only to 1972. In 1974, about 230 metric tons were used,(149) equivalent to 125 metric tons of white arsenic.

Based upon the above discussion, the desiccant and defoliant demand curve (for 1974) was constructed, as shown in Figure 4, as inelastic from $150 to $400 per metric ton of As_2O_3. Above $400, some elasticity is indicated, but it is judged that arsenic acid would still be used to some extent to $700/kkg of As_2O_3. Below $150, the use of arsenic acid should increase to include other cotton-growing areas and to more completely saturate the Texas-Oklahoma region.

In the 1970-1973 period, arsenic acid was priced at about $730 per metric ton (100 percent basis, 1974 dollars). During this period, As_2O_3 was priced at about $200 per metric ton; the As_2O_3 ingredient cost was about $150 per metric ton of arsenic acid.

Demand for Arsenical Herbicides for Weed Control

The monosodium and disodium salts of methanearsonic acid, MSMA and DSMA, are widely used on cotton for weed control. In 1974, about 3.0 million hectares of cotton land were treated with methanearsonates as directed postemergence sprays, in one or two applications, at a level of about 3 kg per hectare per application. An additionl 1.3 million hectares were treated with topical postemargence applications, at about 1 kg/hectare; and 0.2 million hectares were treated prior to crop planting at about 3 kg/hectare.(149) This usage data implies a consumption of close to 10,000 kkg/year. Additional quantities of MSMA and DSMA were used for weed control on turf, on lawns, and on ornamental shrubbery.

Independently, the consumption of methanearsonic acid salts was estimated as:(43,49,150)

Year	MSMA and DSMA, kkg/year	Equivalent As_2O_3, kkg/year
1970	11,000	6,400
1971	9,000	5,200
1972	11,200	6,500
1973	9,100	5,300
1974	9,800	5,700

However, the use of organic arsenicals amounted to only 6.7 percent of all the herbicides used on cotton in 1971, and to only 2.1 percent of all the herbicides used on all crops.(49) One alternative herbicide for cotton, both for preplant applications and as a post-emergent directed spray, is paraquat, which is also used as a harvest aid on cotton.

The prices for MSMA and DSMA have generally been as follows, on a 100 percent basis:(150)

	1968-1969	1975
DSMA Price, 1974 $/kkg	$1,350	$2,200
kkg As_2O_3/kkg DSMA	0.54	0.54
As_2O_3 cost/kkg DSMA, 1974 $	$ 115	$ 155
MSMA Price, 1974 $/kkg	$1,000	$2,100
kkg As_2O_3/kkg MSMA	0.62	0.62
As_2O_3 cost/kkg MSMA, 1974 $	$ 130	$ 180

Figure 4 shows the demand curve for arsenical herbicides. It is constructed to pass through the point of 5,800 metric tons per year of As_2O_3 at a price of $200. The demand is shown to be moderately elastic: at higher prices, the price differential between arsenicals and organics will be smaller; and at lower prices, the arsenicals should command a greater portion of the total herbicide market.

Demand for Arsenical Soil Sterilizers

In 1972, the quantity of sodium arsenite shipped was 4,200 metric tons; compared to 5,300 metric tons in 1967. The prices (in 1974 dollars per kilogram) were $415 in 1972 and $210 in 1967.(151) Since 0.76 kkg of As_2O_3 are equivalent to one kkg of $NaAsO_2$, the ingredient cost per metric ton of sodium arsenite (in 1974 dollars) was $145 in 1972 and $155 in 1967.

The herbicidal uses of sodium arsenite include soil sterilization such as for railroad rights-of-way, for tank farms, for parking lots, for electrical substations, and for ornamental uses under trees and shrubs. The total demand for sodium arsenite, however, includes some insecticide uses such as animal dips and termite control.

The demand curve of Figure 4 indicates that the use of arsenical soil sterilizers is already highly selective, and therefore inelastic.

Demand for Arsenical Wood Preservatives

The demand for chromated copper arsenate (CCA) and for fluor chrome arsenate phenol (FCAP) has been as follows:(45)

Year	CCA, kkg/year	FCAP, kkg/year	As_2O_3 Equiv., kkg/yr		
			CCA	FCAP	Total
1967	1,060	2,430	330	520	850
1968	1,460	1,800	460	390	850
1969	2,120	2,060	670	440	1,110
1970	2,740	1,220	860	260	1,120
1971	3,960	987	1,250	210	1,460
1972	4,430	870	1,330	190	1,520
1973	5,320	767	1,640	160	1,800

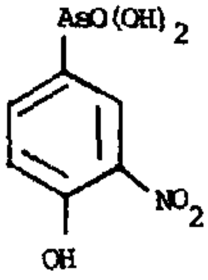
The changeover from FCAP to CCA has also been accompanied by an increase in the total consumption of wood preservatives, in the total consumption of arsenical wood preservatives, and in the consumption of white arsenic. The CCA price, however, has remained fairly stable at about \$2,100 per metric ton of CCA "oxide" (in constant 1974 dollars).(57,152)

For each metric ton of CCA, about 0.45 metric tons of arsenic acid is consumed in its manufacture. At a price of \$750/kkg for arsenic acid (constant 1974 dollars), the arsenical ingredient cost is about \$340. Similarly, the arsenic acid for FCAP is about 0.31 kkg/kkg FCAP, at a cost of about \$230/kkg FCAP. The ingredient cost for copper and for chromium (CCA-B is 20 percent CuO and 35 percent CrO_3) and is more important than the arsenic acid cost.

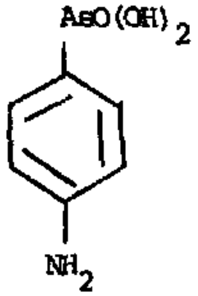
Since no real substitutes can be found for arsenical wood preservatives, and since the cost of arsenical ingredients is a relatively small fraction of the preservative price, the demand curve of Figure 4 has been drawn to be relatively inelastic.

Demand for Arsenical Feed Additives

The two important arsenical feed additives are Roxarsone (4-hydroxy-3-nitrobenzenearsonic acid, or "3-nitro") and arsanilic acid (p-aminobenzenearsonic acid):



Roxarsone



Arsanilic Acid

One metric ton of Roxarsone is equivalent to 0.378 metric tons of As_2O_3; and one metric ton of arsanilic acid is equivalent to 0.459 metric tons of As_2O_3. The consumption and price data are as follows:(153,154,155)

Year	Arsenical Feed Additives, kkg/yr	Equivalent As_2O_3, kkg/yr	Price, 1974 $/kkg	
			Roxarsone	Arsanilic Acid
1968	1,160	464	$6,500	$4,100
1969	1,230	491	6,600	4,000
1970	1,320	528	6,600	3,800
1971	1,300	521	6,800	
1972	1,360	544	6,500	
1973	1,330	531	6,000	
1974	1,360	544	5,500	
1975			4,900	3,300

The cost per metric ton of arsenical feed additive for the arsenic acid ingredient is approximately $425, a small fraction of the product price. The above data indicate that the price of Roxarsone (in constant 1974 dollars) was relatively stable through 1972, but has been decreasing since; the price of arsanilic acid has apparently been dropping steadily.

The substitutes for arsenical feed additives are antibiotics, which range in price from \$20,000 to \$60,000 per metric ton,(153) an order of magnitude greater than the arsenicals. The demand curve of Figure 4 is constructed to be inelastic, reflecting this price differential and also reflecting the relatively small impact of As_2O_3 cost upon feed additive price.

Demand for As_2O_3 in Glass Manufacture

Data on the consumption of As_2O_3 in the glass industry indicate a major reduction from 1968 (5,100 kkg) to 1974 (2,400 kkg). White arsenic was used in the past at a level of about 0.5 percent in decorative glass such as crystal tableware. Substitutes for oxidizing and firing are generally available, so that the demand curve of Figure 4 was constructed to be moderately elastic.

Demand for As_2O_3 in Miscellaneous Uses

This category of use includes specialty items such as As_2S_3 for special pigments, gallium arsenide semiconductors, and arsenide for light-emitting diodes. The special nature of these uses (which now amount to about 500 metric tons per year of As_2O_3) indicates that the demand is inelastic, as shown in Figure 4.

Summary of Demand for As_2O_3

The estimated demand for As_2O_3, as taken from the demand curves of Figure 4, is listed in Table 20. The total estimated domestic demand for As_2O_3 is relatively inelastic from \$100 to \$400 per metric ton. It should be emphasized that the curves of Figure 4 and the data of Table 20 are based upon historical data only in the neighborhood of \$200 per metric ton; extrapolations from this level are based largely upon qualitative information.

Earlier in this section, the conclusion was reached that no long-term (i.e.. ten years) projection of U.S. arsenic supply may be made with any meaningful certainty. The prospect for making meaningful U.S. demand projections is equally bleak for two critical reasons:

TABLE 20

ESTIMATED U.S. DEMAND FOR WHITE ARSENIC (1974 BASIS)

Use	As_2O_3 Demand, kkg/yr, at As_2O_3 Prices (1974 Constant Dollars)								
	$50	$100	$200	$300	$400	$500	$600	$700	$800
Insecticides	6,250	5,830	5,500	5,200	4,800	4,100	2,700	0	0
Dessicants and Defoliants	4,250	3,720	3,500	3,500	3,500	3,130	2,250	0	0
Herbicides for Weed Control	7,150	6,500	5,800	5,150	4,550	3,800	2,400	0	0
Soil Sterilizers	4,450	4,250	4,200	4,200	4,180	3,750	2,800	0	0
Wood Preservatives	1,750	1,560	1,550	1,550	1,550	1,550	1,400	980	230
Feed Additives	1,150	620	550	550	550	550	550	480	140
Glass Additives	3,100	2,780	2,400	2,000	1,610	1,200	630	0	0
Miscellaneous Uses	700	500	480	480	480	480	480	380	100
Total	28,800	25,770	23,980	22,630	21,220	18,560	13,210	1,840	470

1. Arsenical products compete directly with petrochemicals in virtually every use category except for glass additives and some miscellaneous uses. Petrochemical products may be said to dominate the arsenical markets for insecticides, for dessicants and defoliants, for herbicides, for soil sterilizers, for wood preservatives, and for feed additives. The large price increases in 1974 and 1975 for arsenicals were likely the result of large price increases for petrochemicals in these markets. With additional time, it is possible that the production capacity for arsenicals will be increased so that arsenicals can command greater shares of the markets (at lower prices). The volatility of petrochemical prices and supplies, however, would make such projections extremely imprecise.

2. The future for arsenical products lies to a great measure upon actions to be taken by a number of government agencies. The Occupational Safety and Health Administration, the U.S. Environmental Protection Agency's Office of Pesticide Programs, and State agencies have the mechanisms for banning, severely restricting, or otherwise drastically influencing the demand for arsenicals or for their market competitors.

For the above two reasons, historical market data (largely the result of uncontrolled commerce) provide little basis for projecting the future arsenical market, which promises to be a controlled market.

SECTION IX

IDENTIFICATION AND SCREENING OF CANDIDATE CONTROL ALTERNATIVES

In previous sections, the role of arsenic in the U.S. economy has been discussed in detail. The release of arsenic and its compounds to the environment has been addressed, with emphasis upon identifying the specific sources of such releases and upon quantifying these releases. An assessment of the health hazards resulting from such releases has been made.

In this section, various control alternatives for reducing these health hazards are presented, and evaluated from the standpoints of feasibility, necessity, and effectiveness. Those alternatives passing this screening process will be evaluated from a cost standpoint in the next section.

Existing Control Programs

Many suitable control alternatives are already in effect for reducing the dangers from arsenic. These include:

1. The dangers to workers from arsenic exposure are being suitably addressed by the Occupational Health and Safety Administration of the Department of Labor.
2. The potential dangers from arsenic in water supplies are being suitably addressed by the standards for drinking water and by monitoring water supplies, by the U.S. Environmental Protection Agency and by State and local governments.
3. The potential dangers from arsenic in food supplies are being suitably addressed by the standards and monitoring activities of the Food and Drug Administration.
4. The U.S. Environmental Protection Agency and State agencies are active in limiting arsenic discharges via wastewater effluents from point sources. As the results of the study show, arsenic in wastewaters are the least of all emissions and dissipations.

5. The Office of Pesticide Programs of the U.S. Environmental Protection Agency, and appropriate State agencies, are active in pesticide registration programs. These programs limit the use of a given pesticide (insecticide, herbicide, defoliant, dessicant, soil sterilizer, fungicide, etc.) to a specific and finite combination for crop (or application) and pest. These programs require positive Government actions for the use of a pesticide in new applications; conversely, the cancellation of a specific pesticide registration is equivalent to a selective use ban. For registered uses, the pesticides must be appropriately labelled, and with information made available as to proper handling, proper use, use precautions, chemical, physical, and biochemical behavior, behavior in or on soils, and toxicological properties.

6. The U.S. Environmental Protection Agency and State and local agencies are active in reducing the dangers from arsenic air pollution. The actions limiting the sulfur oxide emissions from primary copper smelters have been effective in reducing arsenic emissions from these sources. The actions limiting particulate emissions from power generation stations and other stationary sources have reduced arsenic emissions as well. Since the arsenic content of coal is keyed to the sulfur content, actions resulting in the use of low-sulfur coal have also resulted in reduced arsenic emissions.

Control Alternatives for Specific Emissions or Dissipations

Several control alternatives have been formulated to reduce specific emissions or dissipations or arsenic:

1. Requiring all phosphoric acid manufactured in the United States to be processed for arsenic removal prior to its

use in manufacturing fertilizers or any other phosphate products. The technology used for making food-grade phosphoric acid could be adapted.

This candidate control was rejected from further consideration for three reasons.

First, the arsenic in fertilizers, dissipated on land, has been shown to present no imminent hazard. Second, the arsenic in animal feed phosphates has not resulted in dangerous additions to the human food supply. Third, the arsenic in phosphate detergents, while constituting the largest source of arsenic water pollution from point sources, has not led to dangerous levels of arsenic in fresh waters nor to dangerous levels in public water supplies.

2. Banning the intentional use of arsenic as an alloying element in non-ferrous metals.

   This alternative was rejected for two reasons. First, the only hazards appear to be the emissions to the air and the wastes destined for land disposal in the secondary metals processes. These losses are more directly and appropriately controlled with specific air and land regulations than with a blanket ban. No health hazard is apparent from the use of products (batteries, cables, radiators) containing arsenic. Second, the arsenic alloys serve useful commercial purposes, and substitutes for arsenic alloys are not apparently available.

3. Banning the intentional use of arsenicals in consumer products (other than non-ferrous alloys). These would include arsenical wood preservatives, arsenical fungicides for vinyl plastics, and arsenical herbicides in home-lawn-care products.

This alternative was rejected because there is no apparent health hazard to the consumer via vaporization, leaching, or other mechanism.

4. Stringent emission standards for the release of arsenic trioxide to the atmosphere from high-temperature industrial processes. It is now generally accepted that airborne arsenic trioxide is a carcinogen. The primary copper industry, other primary and secondary non-ferrous metals industries, cotton trash incinerators, and some glass manufacturing plants, all emit arsenic trioxide from high-temperature processes. It was concluded from this study that even the best of the dry dust collection techniques fall far short of effective As_2O_3 capture.

   This control alternative is deemed to be needed, feasible, and effective in reducing health hazards so that it will be considered further. Based upon the technology of As_2O_3 removal from flue gases (as demonstrated in the gas-cleaning parts of byproduct sulfuric acid plants at copper smelters and other non-ferrous metal smelters), high pressure-drop venturi scrubbers can achieve 99+ percent removal of As_2O_3. The control measure, therefore, would be an air quality standard based upon such high removal efficiency.

5. Stringent emission standards for the release of arsenic trioxide to the atmosphere from the combustion of fossil fuels.

   The rationale for this alternative is the same as for the previous alternative, in terms of reducing health hazards. The feasibility of an emission standard for stationary sources, based upon the very high As_2O_3 removal capability of high pressure drop wet scrubbing systems, is similar to that for industrial sources of As_2O_3 air pollution. This alternative will therefore be further considered.

However, it does not appear that a stringent As_2O_3 emission standard for mobile sources is feasible. Moreover, the quantity of emitted arsenic estimated from petroleum combustion, 108 metric tons per year, while significant, is not an extremely large fraction of the total atmospheric emissions of arsenic. Hence, a control alternative for mobile sources of air pollution will not be further considered.

6. Regulating the land disposal of arsenic-bearing slags, flue dusts, sludges, and other residuals from industrial sources.

Large quantities of arsenic and its compounds are in the form of industrial and commercial wastes destined for land disposal. These slags, sludges and collected flue dusts are derived from the primary and secondary non-ferrous metals industries, from the primary ferrous metals industry, and from the phosphorus chemicals industry. The wastes are of varying physical forms, chemical forms, and concentrations of arsenic; and represent correspondingly varying dangers to the environment. Almost always, arsenic is but one of several or many hazardous constituents in these land-destined wastes; toxic heavy metals often accompany arsenic and add to the dangers. The mechanisms for transport into the environment include leaching and runoff into surface and ground waters and transport of finely-divided dusts via wind.

The regulations should ensure that arsenic-bearing industrial wastes destined for land disposal be treated and disposed of in environmentally-adequate ways. The determination of what such adequacy entails is complex, as the following discussion indicates.

General purpose landfills are characterized by their acceptance of a wide variety of wastes and by the usual absence of special containment, monitoring, and leachate treatment provisions for hazardous wastes. The potential for environment damage by landfilled hazardous wastes differs depending on both the composition and quantity of that waste. Many general purpose landfills will accept small quantities of hazardous wastes, particularly if they are in drums or plastic containers, but refuse large amounts. When the hazardousness level is relatively low, due either to the inherent characteristic of the compound or its low concentration in the overall waste mass, even large quantities of hazardous wastes may be accepted. Some arsenic-bearing slags may be disposed of in general purpose landfills; since the arsenic constituent may be at a very low concentration, it may be virtually insoluble (as a stable arsenate, for example), and it may be in a fixed physical form (in a stable aggregate, for example).

Each general purpose landfill has its own ambience - geologically, hydrologically, and environmentally. Ideally, a general purpose landfill would be located in an isolated, dry part of the country with a thick layer of impermeable soil between the waste and the water table. Such areas are plentiful in the western part of the U.S., but not in the east. However, many existing and future landfill sites throughout the U.S. can approach conditions which would classify them as approved landfills, by meeting the following criteria:

(a) The composition and volume of each hazardous waste is known and approved for site disposal by pertinent regulatory agencies.

(b) The site should be ambiently suitable for hazardous wastes.

(c) Provision is made for monitoring wells, rain water diversion, and leachate control and treatment, if required.

The advantages of approved landfill sites include:

(a) Many hazardous wastes may be disposed of in a controlled and environmentally safe fashion.

(b) Selection of landfill sites and disposal technology for ambience suitability still leaves a great number of available landfill sites.

(c) Disposal costs, for both transporting the waste to the site and the landfilling itself, are kept to levels close to those for general purpose sites and still much lower than for secured landfill.

From a practical standpoint many local regulatory agencies and landfill site owners are informally practicing much of this discrimination by selective acceptance of waste materials. Sites with known high potential for surface and ground water contamination are thereby avoided.

Secured landfills involve additional safeguards beyond those described for approved landfills. Criteria for secured landfills include:

(a) The composition and volume of each extremely hazardous waste is known and approved for site disposal by pertinent regulatory agencies.

(b) The site should be geologically and hydrologically approved for extremely hazardous wastes. Included in the criteria would be a soil or soil/liner permeation rate of less than 10^{-7} cm per sec, a water table well below the lowest level of the landfill, and adequate provision for diversion and control of surface water.

(c) Monitoring wells are provided.

(d) Leachate control and treatment (if required).

(e) Records of burial coordinates to avoid any chemical interactions.

(f) Registration of site for a permanent record once filled.

A number of landfills which meet the physical requirements (if not all the regulatory criteria) are located around the country. California has a number of Class 1 impermeable landfills which accept extremely hazardous materials. Texas has similar sites. A number of low level-radioactive waste landfill sites accept industrial hazardous wastes. In addition to the radioactive waste sites various other private secured landfills also take extremely hazardous wastes. At the present time secured landfills are scattered and not fully utilized. Part of the lack of utilization stems from the fact that the majority of the sites are in isolated western areas away from industrial centers. Another reason for the lack of utilization is the high cost as compared to other available disposal methods.

Relatively isolated impermeable soil conditions exist in many areas of the country. If impermeable soil is not available then clay, special concrete, asphalt, plastic and other liners and covers are available to accomplish similar containment and isolation of wastes.

A number of practices are being used to ensure the environmental adequacy of hazardous waste disposal.

Direct hazardous wastes encapsulation in concrete is now practiced by at least one contract disposer. The practice is used for small quantities of containerized miscellaneous hazardous wastes.

Steel drums, alone or with plastic liners, not only provide some long-term containment but also are the most convenient storage and transportation for relatively small quantities of wastes. The ultimate problem involved is the eventual decay of the steel drums. Therefore, unless disposed of in an appropriate landfill site, future release to the environment is likely.

In wet climates, sections of or entire landfill areas are encapsulated by adding clay or asphalt "caps" or "covers" to impervious isolation cells or landfill liners.

The impervious cover is necessary to protect the hazardous waste from rainfall flooding. Neutralizing or pH control ingredients such as lime may also be used to encase or surround the hazardous waste to avoid solubility, decomposition or other change in the character of the waste to increase its environmental damage.

In dry climates, there is no need to encapsulate the entire landfill since rainfall and water buildup is not a problem. Isolation cells may still be constructed, however, for specific hazardous waste containment.

In wet climates, particularly, both private and public landfills are paying increasing attention to leachate collection, monitoring and treatment. Landfill areas in the State of Pennsylvania are representatives of those in a wet climate and leaching treatment has been initiated in some public landfill areas. The vast majority of the landfill operations handling hazardous wastes, however, do not have any leachate control and treatment provisions.

Hazardous sludges are being increasingly treated either on-site or in collection areas by mixing them with inorganic chemicals and catalysts to set up the entire mass into solid structures with low leachability and good land storage or landfill characteristics. There are a number of such processes which produce solids ranging from crumbly soil-like materials to concrete to ceramic slags.

Once a landfill area has been isolated from surface and groundwater contact and leachates are being handled satisfactorily, almost any non-flammable, non-explosive and non-air polluting hazardous waste can theoretically be disposed of safely. There are a number of practical restrictions, however, to this approach:

(a) In wet climates the impervious landfills are flooded with heavy rainfall. Dumping of liquids or sludges into the landfill only accentuates the problem.

(b) Some hazardous wastes create hazards for landfill personnel or give air pollution problems.

(c) Chemical interactions with both other materials and the liner can cause undesirable side effects.

Control Alternative Aimed at the Commercial Use of White Arsenic

The most direct control alternative is a ban on white arsenic consumption, either on the basis of selective uses, or upon all uses (i.e., a total ban). There are several strong arguments against banning white arsenic use:

1. Any actions directed at commercial white arsenic and its derivatives, even if totally effective in halting all emissions and dissipations related to commercial uses, would only address a small fraction of the total arsenic quantities mobilized in our economy. Much more arsenic is unintentionally mobilized than is intentionally mobilized.

   Of all the arsenic that is mobilized, the comparatively small quantity intentionally used is the only portion that serves useful purposes in our society.

2. Even if such actions could be effective in halting emissions and dissipations, they could not be justified (except for the case of airborne emissions) in terms of demonstrated health hazards. The data gathered in this study indicate the opposite: that arsenic in water, in food, in the soil, and generally dissipated in the environment as it is now presents no identifiable health hazard.

However, the emissions to the air from the intentional commercial use of white arsenic are sizable and do involve a potential hazard to health. There is sufficient justification, therefore, to retain the alternatives (for further consideration) of selective or total bans upon white arsenic use.

The one exception is the use of white arsenic for very small-volume and specialized items. These are included in the "miscellaneous uses" category in this report, and include semiconductors, light-emitting diodes, and special glasses for infrared applications. The health hazards from such uses appear negligible, while the usefulness of arsenic appears quite important.

Needs for Additional Research

One of the results of this study is that very large quantities of arsenic are mobilized by the primary iron and steel industry. Further research is needed to validate the quantity estimates made in this study; to validate the hypotheses made in this study of the distribution of the arsenic to end products, to land, to water, and to the air; and to determine the environmental adequacy of the widespread use of arsenic-bearing steelmaking slags.

This study made apparent that several emerging technologies will mobilize very large quantities of arsenic, comparable in magnitude to all the arsenic mobilized by existing commercial activities. These emerging technologies are coal gasification, oil shale processing, and geothermal energy recovery. Since the Government is playing an active role in the research and development of these emerging technologies, appropriate Government agencies (Environmental Protection Agency, Energy Research and Development Agency, and Department of the Interior) could take the initiative in developing effective arsenic removal and disposal techniques as integral parts of these processes, highlight the fate of arsenic in Environmental Impact Statements, and develop appropriate regulations as the technologies emerge.

The application by spraying of arsenical pesticides results in relatively large quantities atomized or evaporated. Since airborne arsenic trioxide is an identified danger to human health, further research is deemed necessary to quantify the hazards to the general population (other than farm workers) from such practices, and to seek techniques for pesticide application which reduce the quantities lost to the atmosphere or which reduce the range of travel of these airborne pesticides.

SECTION X

COSTS OF ALTERNATIVE REGULATIONS

Bans Upon White Arsenic Use

The most direct control alternative upon the commercial flow of white arsenic and its compounds is a ban upon its use. Such a ban can be all-encompassing, or it can be for selective uses. This section is intended to estimate the costs of such bans, to provide information (along with a separate assessment of the feasibility, effectiveness, and benefits of such bans) for evaluating alternatives.

The costs estimated for each control alternative are in terms of dollars per kilogram of white arsenic diverted from dissipation via the use in question. A comparison of control options on the basis of dollars per kilogram of white arsenic diverted is potentially misleading unless recognition is made of the benefits to human health and to environmental quality from each such diversion. The eventual choice of control measures should ideally be based upon the cost per unit reduction in health damage. Although the correlation between quantities of white arsenic emitted and health damage has been discussed, the basis for a quantitative estimate of health damage does not yet exist. For the purposes of this section, therefore, the benefits of a control alternative will be assessed in terms of quantity of white arsenic diverted from dissipation, with the results regarded as the results of a screening mechanism of candidate options. Without a more precise measure of health benefits, it is not possible to identify the most cost-effective options or to determine the amount of diversion societally desirable. The purpose of this section is to provide an indication of the available options, their likely effects, and the probable costs — important steps in selecting controls to be instituted.

The control options evaluated here are those which seemed most feasible in preliminary review. Many alternatives were considered and some were rejected for detailed analysis because the costs appeared too great for the perceived benefit on an a priori basis; others were rejected because their effectiveness was shown to be too small.

The costs of a control alternative can be broken into two broad categories. Long-run costs are derived from the differences between the two "steady states", one without a control alternative and one with; these costs extended indefinitely. The short-run costs are those incurred while moving from the steady state without a control alternative to one with a control alternative; these costs have a termination when the steady state with a control alternative is reached.

A second important distinction among costs is that between those involving direct monetary outlays and those which are felt in other ways. If an emission standard were adopted, then the control and treatment cost is an out-of-pocket expense. If the quantity produced decreases, however, then the foregone consumer surplus is a cost despite the fact that there is no direct monetary outlay.

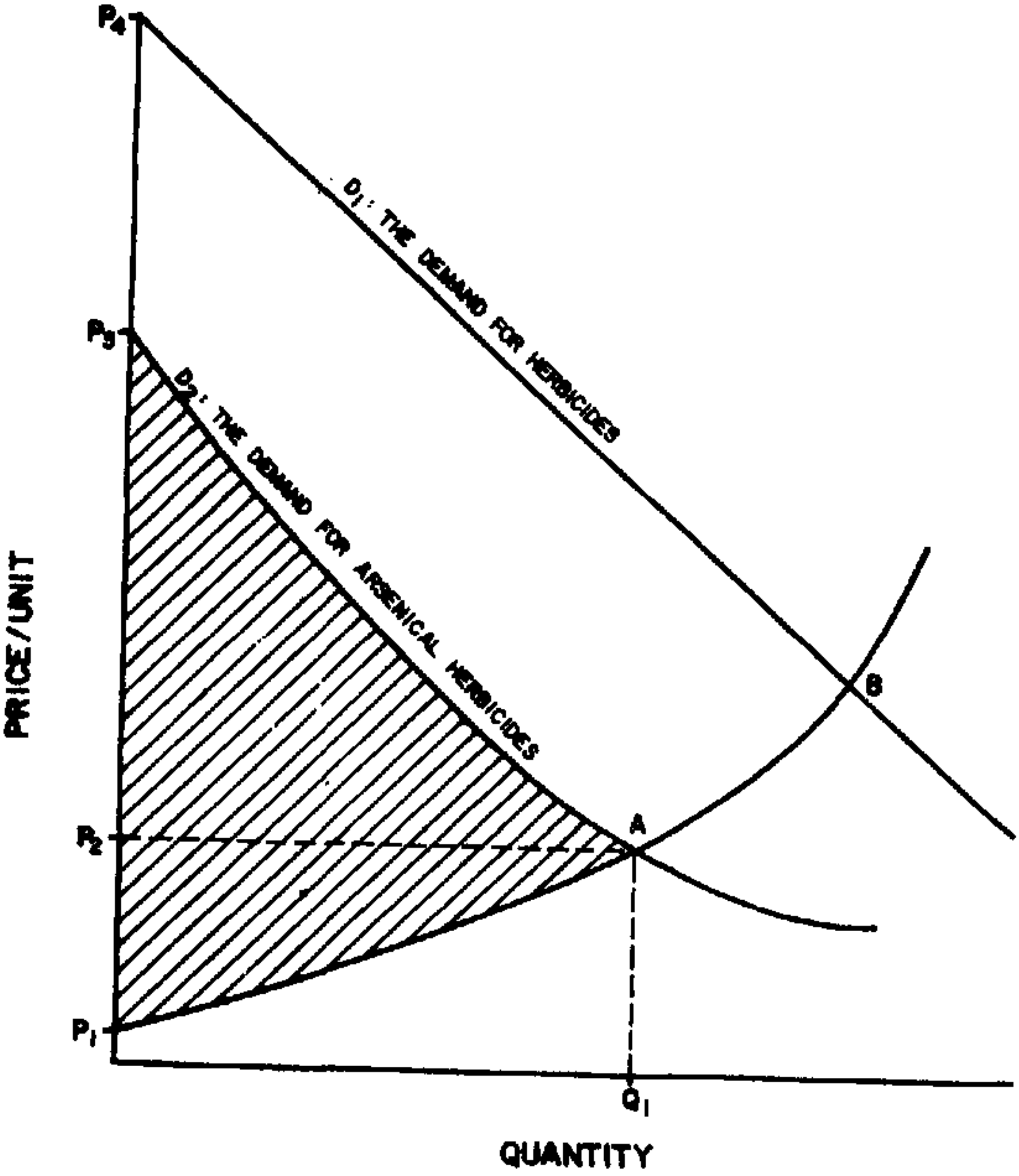
A ban on white arsenic and its derivatives results in a cost in forcing people to use substitutes; e.g., in forcing users to forego the benefits of arsenicals over and above the next best substitute. Although there are substitutes in virtually every major use of white arsenic, they are not perfect substitutes. Sometimes they cost more, sometimes they don't provide the same quality product, and sometimes they don't last as long. The mere fact that white arsenic is being used verifies that it has advantages over the next best substitutes. It is possible that some uses are not justified at current market prices, but it is inconceivable that all uses are unjustified.

The long-run cost to society of foregoing the present and future benefits of arsenical products is called the foregone benefits cost, and occurs each year a ban is operative. It is made up of the foregone benefits to users and the foregone benefits to producers. The former is the difference between the market price and the value of white arsenic in various uses (the amount that users would have been willing to pay to have white arsenic available for each purpose.) The latter is the difference between the market price and the cost of producing white arsenic for the market.

Figure 5 is a simple market description illustrating foregone benefits from a ban which prohibits the Q_1 consumption of white arsenic for, say, herbicides. Users forego benefits equal to area P_2P_3A while producers forego benefits equal

FIGURE 5

FOREGONE BENEFITS



to area P_1P_2A. In other words, users pay only the P_2 market price, but the actual value/unit of arsenic to them is the average value on the demand curve between P_3 and A. Likewise, producers receive price P_2, but the average cost/unit is only the average value on the cost curve between P_1 and A.

By determining the value of white arsenic from demand curves, we automatically consider the possibility of white arsenic substitutes. The difference between the D_1 specified demand for herbicides and the lower D_2 demand for arsenicals as a specific herbicide reflects opportunities for substitutes. Stated otherwise, the foregone benefits to users from a ban on white arsenic would be P_2P_4B instead of the smaller P_2P_3 if arsenic had no substitute. Moreover, the slope of the demand curve D_2 is determined by the relative price, availability, and effectiveness of substitutes. However, although presently-available substitutes are represented in the demand curve, new substitutes that could be developed are not generally included, even though they can reduce the long-run foregone benefit cost significantly.

There are two basic ways to determine foregone benefits to white arsenic users and producers. One approach is an engineering analysis—an analysis that a user himself would employ in determining what he is willing to pay for white arsenic and its substitutes, or that a producer himself would employ in determining how much to produce at each price. A second approach is to trace out the demand curve (e.g., the curve P_3A in Figure 5) from (1) observed changes in market prices and quantities and (2) opinions of experts among suppliers and consumers.

The estimates for this study were developed under the second approach. The first approach is very expensive and subject to significant errors from inaccurate or incomplete information.

Arsenic demand curves developed for this study indicate that substitutes for most uses are much more expensive or are so inferior that the current \$200 per metric ton market price could increase to \$700 to \$800 per metric ton before users would completely cease using arsenicals. By definition, the white arsenic user who would pay as much as \$700 per kkg would forego a minimum of \$500 benefit per metric ton if the As_2O_3 he can now purchase at \$200 per kkg is banned.

The white arsenic demand curve P_3A in Figure 5 is drawn to indicate that market price is nearly equal to consumer value for part of the uses, but consumer value is significantly above market price in other uses.

In the long run, foregone benefits are paid by the many consumers of products in which white arsenic is a component. It is erroneous to think that the benefits of white arsenic uses are obtained by a few producers acting against the public interest while the benefits of less arsenic pollution are to be enjoyed by the general public. In the short run, producers of arsenicals and manufacturers that use arsenicals in their products will suffer losses from a ban. However, in the long-run, suppliers reach a new equilibrium via copper prices and the consumers bear the loss of foregone benefits via higher copper prices and via higher prices or lower quality of products containing substitutes for white arsenic.

Estimates of foregone benefits are certainly subject to error. However, they are often a significant cost to society whenever there is a ban on products for environmental or any other reason; therefore, foregone benefits must be estimated to provide a complete accounting of social costs and they must be analyzed if we expect to make rational decisions on arsenic controls. Estimates in this report are objective estimates of cost consequences of specified arsenic control alternatives.

Another long-run cost, in addition to the foregone benefits cost, is the cost of disposing of the excess white arsenic in environmentally-adequate ways. Since white arsenic is a byproduct, As_2O_3 and its derivates which cannot be sold (because of a ban on use) must continuously be collected and disposed of in a secured landfill. It should be pointed out that, by placing a ban on a certain form of consumption, total domestic production is unlikely to fall by an amount equal to that form of consumption. Slacks in demand are more likely to result in decreased imports. Carried further, sufficient slacks in demand would result in exports of white arsenic. This aspect further confuses an estimate of this cost.

There are several types of short-run costs that must be accounted for:

1. Capital that becomes obsolete or reduces in value — If arsenicals are not available for a specific production process, then either the capital will be used for other purposes in its present state, it will be converted for other purposes, or it will lie idle, depending upon the costs of conversion and the perceived productivity of the capital in a new function. The cost of a white arsenic ban to society depends upon how much of the benefits which could have been provided by the existent capital can be reclaimed. By introducing a time lag between the announcement of a ban and its institution, these costs can be reduced significantly.

2. Unemployment — As a specific production is halted by a ban on white arsenic, the labor involved in that production could become unemployed. The cost depends upon the amount of time unemployed and their productivity in new jobs relative to the old jobs. By introducing a time lag between the announcement of a ban and its institution, these costs can be reduced significantly.

3. Stockpiling — If the demand for white arsenic is reduced, stockpiling is likely to occur as a short-run response. The cost is the opportunity cost of using the resources which go into stockpiling. The drop in demand will result in fewer imports and a short-run stockpiling at the smelter for a selective ban. For a total ban, stockpiling would probably not occur since the smelters would have no reason to refine the white arsenic to stockpile.

   Because an estimate of the amount stockpiled is dependent on so many unknown variables, this cost will not be quantified. However, since the cost is probably small and it only exists in the short-run, this will not affect the results appreciably.

Using the above outline as a guide, the long-run and short-run costs resulting from a selective ban on each of the primary uses of white arsenic will be considered, as well as a total ban on all forms of white arsenic consumption.

Estimation of Foregone Benefits (Long-Run Costs)

Using the estimated white arsenic demand curves of Figure 3, the foregone benefits of ban on each of the uses was calculated as the area between the demand curve and the supply curve. The results are tabulated below in terms of the annual foregone benefits for each selective ban, and the foregone benefits per kilogram of arsenic trioxide diverted for each ban. The miscellaneous uses of white arsenic were not included in this analysis, as substitutes are not generally available for specialized uses.

As_2O_3 Use Ban Assumed	As_2O_3 Diverted kkg/year	Foregone Benefits, Million Dollars/yr	Foregone Benefits $/kkg Diverted
Insecticides	5,500	$ 2.94	$530
Dessicants and Defoliants	3,500	2.01	570
Herbicides (Weed Control)	5,800	2.87	500
Soil Sterilizers	4,200	2.33	560
Wood Preservatives	1,550	1.06	680
Feed Additives	550	0.41	740
Glass Additives	2,400	1.11	460
Total Ban	23,500	$12.73	$540

The foregone benefits per metric ton of white arsenic diverted amount to $540 for a total ban, and to approximately that amount for individual bans upon the agricultural uses. The foregone benefits per metric ton are somewhat lower for glass additives (reflecting the moderate elasticity of this curve in Figure 3); and are somewhat higher for wood preservatives and feed additives (reflecting the inelasticity of these curves in Figure 3).

Estimation of Disposal Costs for Excess As_2O_3 (Long-Run)

The 1974 domestic white arsenic production was estimated at 8,700 metric tons. The total domestic demand for white arsenic (24,000 metric tons in 1974) would not be reduced to the point where domestic production would be curtailed for any one individual use ban; it appears reasonable that reduced imports would be the result of any single ban. Hence, there would be no disposal cost associated with any single assumed use ban.

However, a total ban on white arsenic would mean that the 8,700 metric tons must be disposed of in an environmentally-adequate manner. A unit cost for such land disposal (i.e., secured landfill), including transportation, is about \$50 per metric ton,(75,123,136) so that the total cost would be \$435,000 per year. In lieu of analyzing the world market to determine if any or all of the excess white arsenic could be exported, the maximum costs for disposal will be assumed.

Estimation of Short-Run Costs for As_2O_3 Use Bans

The short-run costs for a ban on white arsenic include the idle capital and unemployment in the manufacture of white arsenic, and the idle capital and unemployment in the industries using white arsenic.

The 1967 and 1972 Census of Manufacturers for SIC 2819, Industrial Inorganic Chemicals, N.E.C. (in which white arsenic manufacture is classified); and for SIC 2879, Agricultural Chemicals, N.E.C. (in which most arsenical products are classified); contain the following statistics:(151,156,157)

	Value of Shipments Million Dollars	Number of Employees	Payroll, Million Dollars	Gross Value of Fixed Assets, Million Dollars
SIC 2819, 1972 Census	3,657.5	60,600	666.9	-
SIC 2819, 1967 Census	4,248.4	81,200	662.4	-
SIC 2879, 1972 Census	1,150.8	12,200	116.5	-
SIC 2879, 1971 ASM	963.9	11,900	102.6	410.5
SIC 2879, 1970 ASM	859.0	12,200	101.9	410.5
SIC 2879, 1969 ASM	976.7	12,300	94.6	374.4
SIC 2879, 1968 ASM	902.4	12,100	85.2	314.6
SIC 2879, 1967 Census	817.0	11,500	80.7	272.9

These statistics were converted into the following average ratios:

a) 14 employees per million dollars/year of shipments

b) Annual wages per employee are about $10,000.

c) The gross value of the fixed assets are 40 per cent of the annual value of shipments.

Applying these ratios to the manufacture of white arsenic, where the value of shipments in 1974 (8,700 kkg at $200/kkg) was $1.74 million, yields the following values:

25 employees
$250,000 annual payroll
Gross Value of fixed assets = $700,000

Since the domestic white arsenic production is only 36 percent of the domestic consumption (the balance being imports), only a total ban would result in unemployment or in idle capital (selective individual use bans should instead result in decreased imports). If the average length of unemployment caused by a total ban were one year, the associated unemployment cost would be $250,000. The white arsenic production facilities would probably have no salvage value. On the other hand, these facilities are not new, and the present (depreciated) value, taking into account possible recent additions for pollution control and other reasons, is crudely estimated at $350,000. If this present value is amortized over 5 years, the annual idle capital cost would be $70,000.

Table 21 lists the arsenical derivative products discussed in Chapter VIII, along with their quantities, prices, and value of shipments. The substitutes for these products are organics, and it is assumed that the equipment used for manufacturing the arsenicals could not readily be converted for manufacturing the substitutes and that unemployment would result. Apply the ratios developed above, the arsenical derivatives industries, with a value of shipments of $52.9 million, is estimated to have:

740 employees
$7.4 million annual payroll
Gross Value of fixed assets = $21.2 million

Table 21

Economics of Arsenical Derivative Products 1974 Basis

Product	Quantity kkg/year	Avg. Price $/kkg	Value of Shipments *Million Dollars/Year*	Employees	Annual Payroll	Fixed Assets	Unemployment Costs (6 mos)	Idle Capital Costs/Yr *(10 yrs)*
Insecticides	11,700	625	7.3	100	$1,000,000	$ 2,900,000	$ 500,000	$ 290,000
Dessicants	4,400	730	3.2	45	450,000	1,300,000	225,000	130,000
Herbicides	9,800	2,100	20.6	290	2,900,000	8,300,000	1,450,000	830,000
Soil Sterilizers	4,200	415	1.7	25	250,000	700,000	125,000	70,000
Wood Preservatives	6,000	2,100	12.6	175	1,750,000	5,000,000	875,000	500,000
Feed Additives	1,360	5,500	7.5	105	1,050,000	3,000,000	525,000	300,000
Total	37,460	-	52.9	740	$7,400,000	$21,200,000	$3,700,000	$2,120,000

The short-run costs are estimated based upon a 6-month employment period; and upon a present value of assets equal to 50 percent of the gross value and a 5-year amortization period for this present value. The results of this estimation are shown in Table 21.

More precise estimates of the short-run costs would of course be desirable, but the error should not affect the final cost estimate appreciably.

Summary of the Costs for Banning White Arsenic Use

Table 22 summarizes the costs for each selective ban and for a total ban on arsenic use. As Table 22 shows, the foregone benefits are the predominant costs for all but feed additives (where the value added is very large compared to the arsenical raw material cost).

For a total ban on arsenic use, the overall first-year costs would be \$20.0 million. The costs for each of the next four years would be \$16.0 million, and the annual costs thereafter would be \$13.2 million.

Based upon a consumption of 24,000 metric tons of white arsenic, the costs of a total ban per metric ton of white arsenic are \$830 for the first year, \$665 for the next four years, and \$550 thereafter.

Costs of Controlling Industrial Arsenic Emissions to the Atmosphere

The most important need for additional controls is the reduction of arsenic trioxide emissions to the atmosphere from high-temperature industrial processes. The primary copper industry is the largest source of such emissions; an estimated 6,300 metric tons per year of As_2O_3 are emitted. The total As_2O_3 in copper roasting and smelting flue gases amounts to an estimated 30,000 kkg/year, implying that 23,700 kkg/yr are collected and that the collection efficiency is 79 per cent. An additional 11,600 kkg/yr of As_2O_3 in converter flue gases are removed in byproduct acid cleaning plants.

The roasting and smelting flue gases are typically passed through dry dust collection systems, which fall far short of effective (i.e., 99+ per cent) As_2O_3 capture. Some high-residence-time devices such as "balloon flues" are used but also with limited success. It appears that high-pressure drop venturi scrubbing

Table 22

Summary of Costs of Selected and Total Bans
Costs in Millions of 1974 Dollars Per Year

As_2O_3 Use Ban Assumed	Long-Run Costs		Short-Run Costs	
	Foregone Benefits	Disposal	Unemployment (First Year Only)	Idle Capital (Five Years)
Insecticides	2.94	-	0.50	0.29
Dessicants	2.01	-	0.23	0.13
Herbicides	2.87	-	1.45	0.83
Soil Sterilizers	2.33	-	0.13	0.07
Wood Preservatives	1.06	-	0.88	0.50
Feed Additives	0.41	-	0.53	0.30
Glass Additives	1.11	-	-	-
As_2O_3 Production	-	0.44	0.25	0.70
Total Ban	12.73	0.44	3.97	2.82

systems are the technically-feasible controls for As_2O_3 in these flue gases. Such systems are used in cleaning the converter flue gases prior to manufacturing sulfuric acid, and are effective to the point where the commercial acid contains only 0.5 ppm arsenic,(158) implying 99+ percent removal of As_2O_3. The following analysis leads to an estimate of the costs for controlling As_2O_3 emissions from copper smelters.

The sulfur/copper ratio in copper concentrates is nominally about 1.15, and about one-third of the sulfur is lost in the roasting and reverberatory (smelting) steps. SO_2 in these flue gases is nominally at about a 4 percent volumetric concentration, although newer plants are being designed to yield higher SO_2 concentrations so that it may be captured more economically. For the conventional plants, the above data permits the estimation of the quantity of flue gases from roasting and smelting: about 6,700 cubic meters (STP) per metric ton of copper. If these gases are passed through a waste heat boiler and an electrostatic precipitator, they should be at about 250°C and 1 atmosphere, so that the gas volume prior to wet scrubbing would be about 13,000 actual cubic meters per metric ton of copper.

A "typical" smelter is defined as having an annual copper production of 100,000 metric tons (there would be 16 such typical smelters equivalent to the current U.S. copper production of 1.6 million metric tons). The throughput of this typical smelter is on the average about 0.20 metric tons of copper per minute; the roasting and smelting flue gas flow rate would then be 2,600 actual cubic meters per minute (92,000 actual cubic feet per minute).

The 1967-68 total capital cost (purchase cost plus installation cost) for a high-efficiency (99.5 percent) venturi scrubber with a capacity of 92,000 ACFM was $220,000.(159) Updating this cost to 1975 with the Chemical Engineering Plant Cost Index results in a capital cost of $365,000. The annual operating cost is about 5 percent of the total capital cost, or about $20,000 per year.(159)

The scrubber liquor would likely be recirculated, with a relatively small fraction bled for removal of arsenic and other contaminants. Hypothetically, the scrubber bleed may be treated with lime followed by sedimentation; alternately, it may be treated with sodium sulfide or sodium hydrosulfide (as in food-grade phosphoric acid manufacture) with subsequent removal of As_2S_3 by filtration. Such a conventional system for treatment of the scrubber bleed should cost approximately $150,000 (installed) for the "typical" plant; with annual operating costs of perhaps $20,000.

The "typical" plant would then have solid wastes from the scrubber liquor treatment of perhaps 500 metric tons per year. At a disposal cost of $50 per metric ton in a secured landfill, these costs would amount to $25,000 per year. In this analysis, no credit will be taken for possible recovery values from these wastes.

In summary, then, this "typical" plant would have overall capital costs of about $515,000 and annual operating costs of about $65,000. For the entire primary copper industry, made up of 16 such typical plants, the costs for removal of most of the 6,300 metric tons per year of As_2O_3 would be a capital cost of $8.3 million and an annual operating cost of $1.0 million. If the capital investment were amortized over 10 years, the total annual cost would be about $1.8 million; or about $300 per metric ton of As_2O_3 removed.

Very little of the As_2O_3 should pass through such a high-pressure-drop wet scrubbing system. In actuality, the major emissions of As_2O_3 should then be attributable to flue gases which never are collected; i.e., the leaks and spurious emissions from the smelting process equipment. Since the total quantity of As_2O_3 in all copper flue gases amounts to about 42,000 metric tons per year, a one percent loss of such gases is equivalent to an emission of 420 metric tons per year.

Costs of Controlling Arsenic Emissions from Fossil Fuel Combustion Stationary Sources

The same control technology, i.e., high-performance wet scrubbing systems, could be applied to the flue gases from electric power generating stations and other stationary sources which burn fossil fuels.

Using a factor of 10 cubic meters (STP) of flue gas generated per kilogram of coal burned,(9) a "typical" power plant that burns 100,000 metric tons of coal per year (190 kg/min) generates 1,900 cubic meters (STP) per minute of flue gas. Assuming a flue gas temperature of 250°C, the flue gas flow rate would be 3,650 actual cubic meters per minute, or 129,000 actual cubic feet per minute.

The 1967-68 total capital investment (purchase cost plus installation cost) for a high-efficiency (99.5 percent) venturi scrubber with a capacity of 129,000 ACFM was \$300,000.(159) Updating this cost to 1975 with the Chemical Engineering Plant Cost Index results in a capital cost of \$500,000. The annual operating cost is about 5 percent of the total capital cost, or about \$25,000 per year.(159)

As in the case for the previous analysis (for the copper smelter), a system for treating and recirculating the scrubber liquor would be required. In a less demanding situation than exists at a copper smelter, the installed cost of this system may amount to \$100,000, with annual operating costs of perhaps \$15,000. The "typical" power plant would then have hazardous wastes from the scrubber liquor treatment of perhaps 100 metric tons per year. At a disposal cost of \$50 per metric ton in a secured landfill, these costs would amount to \$5,000 per year.

This "typical" power plant would have, then, a total capital cost of \$600,000 and annual operating costs of \$45,000. For the entire U.S. population of coal-burning power plants (4,500 such "typical" plants), the required capital cost would amount to an estimated \$2.7 billion, and the annual operating cost to \$200 million. If the capital investment were amortized over 20 years, the total annual cost would be about \$335 million. Even if these costs were apportioned among all the hazardous materials removed by such control systems, an estimated 10 percent accountable to arsenic would be \$33.5 million per year. Since the total quantity of arsenic in present atmospheric emissions from coal combustion is 650 metric tons per year, the costs of such a control measure would be about \$50,000 per metric ton of arsenic removed, or \$39,000 per metric ton of As_2O_3 removed.

Costs of Safe Disposal of Land-Destined Wastes

Large quantities of arsenic and its compounds are in the form of industrial and commercial wastes. Slags, sludges, and collected flue dusts from a variety of sources contain arsenic and other hazardous substances. An estimate of the total waste quantity, the arsenic content, and the total hazardous constituents is:

Source	Total Hazardous Wastes, kkg/year	Total Hazardous Constituents, kkg/year	Arsenic Quantity, kkg/year
Primary Zinc (Pyro)(75)	288,000	47,200	120
Primary Lead Industry(75)	542,000	61,200	800
Primary Copper Industry(75)	6,089,000	95,200	12,000
Other Pri. Non-Ferrous Metals(75)	30,000	500	50
Phosphoric Acid Sludges	1,000	150	90
Manganese Smelting Dusts	5,000	1,000	350
Iron and Steel Dusts(133)	1,951,000	20,000	1,350
Coal Combustion Ash	45,000,000	15,000	1,800
Totals	54,000,000	245,000	17,560

The costs for environmentally-adequate disposal range from 0 to $50 per metric ton of wastes. The lower costs are applicable to slags, where the arsenic and other hazardous constituents may already be chemically fixed (as arsenates, etc.) and so not susceptable to leaching. The higher costs are applicable to lined ponds, impervious landfills, concrete pits, collection and treatment of leachates, surface protection from dispersion of dusts, chemical fixation of sludges and dusts, etc.

In the major non-ferrous primary metals industries (zinc, lead, and copper) the overwhelming majority of the total wastes are slags, rather than sludges or dusts. Costs for environmentally-adequate land disposal have been estimated.(75)

Industry	Metal Production kkg/yr	Disposal Cost Per kkg Product	Disposal Cost/Yr
Primary Copper	1,600,000	$1.29	$2,060,000
Primary Lead	610,000	1.37	840,000
Primary Zinc (Pyro)	290,000	4.20	1,220,000

These costs, and the disposal costs for the arsenic-bearing wastes from other industrial sources, are only partially attributable to the control of arsenic pollution, since other hazardous constituents are in these wastes.

For the primary copper industry, which is the source of three-fourths of the arsenic in all land-destined wastes, the total estimated costs are $2.06 million per year. If these costs are apportioned among all the hazardous constituents (totalling 95,200 kkg/year), the share to be borne by controlling arsenic (13,000 kkg/year) would be $280,000 per year, or about $22 per metric ton of arsenic. Using this unit cost to extrapolate to other sources, the total apportioned cost for environmentally-adequate disposal of arsenic wastes would be about $380,000 per year.

SECTION XI

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