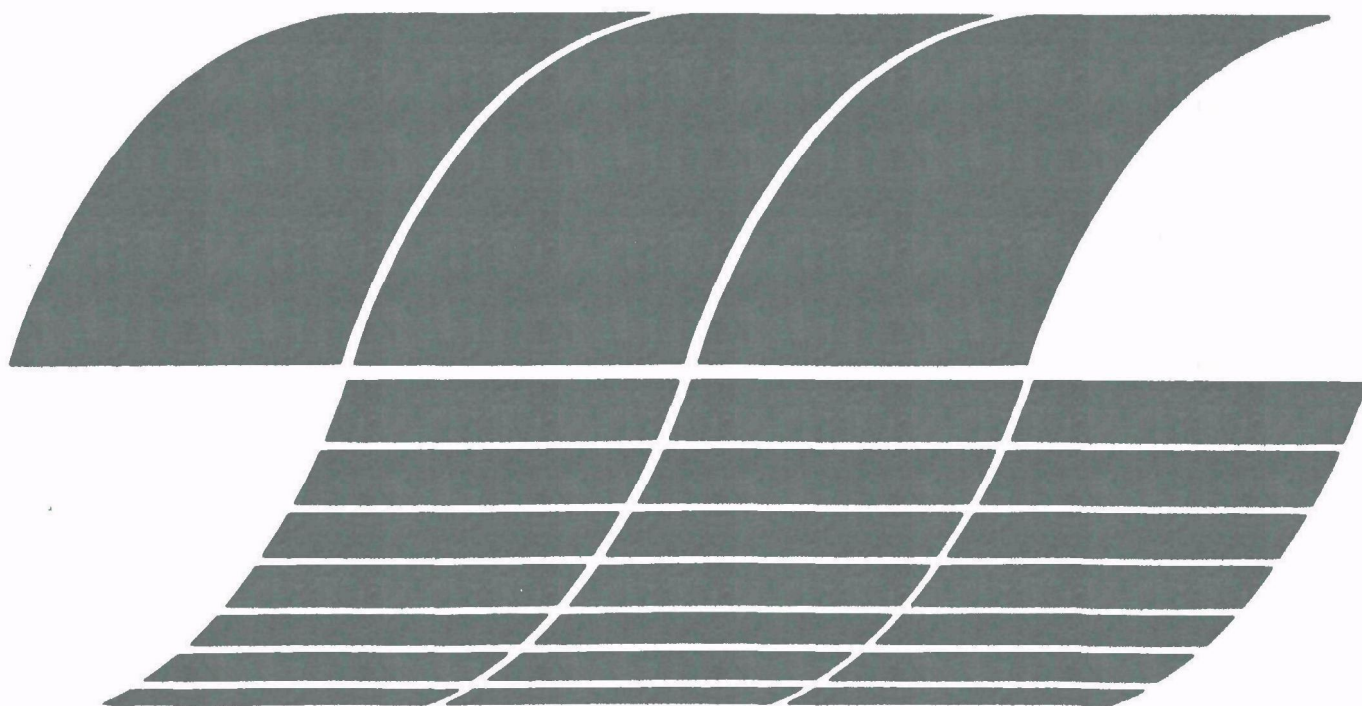




# Criteria for Assessment of Environmental Pollutants from Coal Cleaning Processes

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**June 1979**

# **Criteria for Assessment of Environmental Pollutants from Coal Cleaning Processes**

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## FOREWORD

Many elements and chemical compounds are known to be toxic to man and other biological species. But, our knowledge concerning the levels and conditions under which these substances are toxic is extremely limited. Further, little is known concerning the emission of these pollutants from industrial processes and the mechanism by which they are transported, transformed, dispersed, or accumulated in our environment.

Portions of the Federal Clean Air Act, the Resource Conservation and Recovery Act, and the Federal Water Pollution Control Act require the U.S. Environmental Protection Agency (EPA) to identify and regulate hazardous or toxic substances which result from man's industrial activities. Industrial pollutants are often identified only after harmful health or ecological effects are noted. Remedial actions are costly, the damage to human and other biological populations is often irreversible, and the persistence of some environmental contaminants may endanger future populations.

EPA's Office of Research and Development is responsible for health and ecological research, studies concerning the transportation and fate of pollutants, and the development of technologies for controlling industrial pollutants. As a part of this Office of R&D, the Industrial Environmental Research Laboratory, which is responsible for development of pollution control technology, conducts a large environmental assessment program. The primary objectives of this program are:

- The development of information on the quantities of toxic pollutants emitted from various industrial processes--information needed to prioritize health and ecological research efforts.
- The identification of industrial pollutant emissions which pose a clearly evident health or ecological risk and which should be regulated.
- The evaluation and development of technologies for controlling pollution from these toxic substances.

The coal cleaning environmental assessment program has as its specific objectives the evaluation of pollution and pollution control problems which are unique to coal preparation, storage, and transportation. The coal preparation industry is a mature yet changing industry and in recent years significant achievements have been made in pollution abatement. The environmental assessment work will document existing environmental regulations and the adequacy of commercial pollution control techniques. Hopefully, any potential long range environmental problems which may exist will be identified. Specifically, this report provides preliminary criteria for the assessment of environmental pollutants associated with coal cleaning processes.



## ABSTRACT

The objective of this research was to develop criteria for the assessment of environmental pollutants associated with coal cleaning processes. The primary problem is concerned with emissions of pollutants to all three media--air, water, and land--and assessment of their effects on man and the environment.

The pollutants associated with coal cleaning are primarily inorganic compounds associated with the ash fraction. Lists of potential pollutants from coal cleaning and utilization containing hundreds of entries have been proposed. A group of 51 elements and 23 substances or groups of substances was selected judgmentally from larger lists for investigation.

The fundamental criterion for ranking the importance of any pollutant is the relationship between its expected environmental concentration and the maximum concentration which presents no hazard to man or biota on a long-term basis. Environmental concentrations depend upon emission rates and the effects of physical transport and dispersion. Ultimately, these data will come from field measurements but in the interim must be estimated. Methodology for these estimations are reviewed; the requisite methodology is well developed and little further development appears necessary.

Ecological transport and distribution is much less well developed, and the investigation has revealed that there are large gaps in the data for many elements and many species. Illustrative data are presented for eight of the most important trace elements.

Twenty formulae for deriving estimated permissible concentrations (EPC's) were identified and considered in this study. No one formula was found to fulfill all needs; recommendations were developed for suggested improvements. A major deficiency in all formulae is the inability to utilize the variety of pertinent toxicological data available. Improved methods are badly needed for interconversion of toxicological data to more useable

forms. Equations have been developed for conversion of toxicological data for four non-oral routes of administration to an LD<sub>50</sub> basis.

This preliminary investigation has shown that the problem of an adequate health and toxicological effects data base equals or exceeds the methodology problem. One of the most critical information needs to support the derivation of EPC's are dose-response data on the health and ecological effects of individual pollutants and their mixtures. Data are sparse on the pollutants of concern to coal cleaning, and much more research needs to be done in this area.

This report was submitted in partial fulfillment of Subtask 242 of Contract No. 68-02-2163 by Battelle's Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period from November 8, 1976, to October 30, 1978, and work was completed as of December 30, 1978.

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## 1.0 EXECUTIVE SUMMARY

### 1.1 Introduction

The fundamental criterion for assessing environmental pollutants associated with coal cleaning is the relationship of the permissible environmental concentrations to those which actually can or do occur. Elucidating this relationship involves determining a number of factors, some of which are complex:

- (1) The pollutants most needing control need to be identified, either because of the quantities emitted or their toxicities, or both. Also, almost by definition, substances designated as pollutants by EPA are candidates for control. Identification of the pollutants most needing control is a basic objective of this study. The pollutants likely to be associated with coal cleaning are discussed in Section 3.1. Also important are the ever-changing Federal and state environmental regulations governing the emission of pollutants; the current status of those regulations likely to affect coal cleaning processes are discussed in Section 3.2.
- (2) Data on the quantities and concentrations of those pollutants emitted to the environment are needed. These data come from other subtasks analyzing the process steps (coal cleaning, handling, transportation, storage, and combustion). The approach to this problem is discussed in Section 4.1.
- (3) Estimates of environmental concentrations of pollutants in all three media--air, water, and land--are needed. This estimation initially involves physical transport and dispersion; the approaches to modeling physical distribution are discussed in Section 4.2. Ecological transport and distribution is much less well-studied; there are large gaps in the data for many elements and many species. Qualitatively, the pathways and mechanisms for accumulation and dispersal have been identified;

the problems arise in attempting to quantify these mechanisms. The approach to these problems and several illustrative examples are described in Section 4.3.

- (4) One of the most critical information needs is data on the toxicities of the individual pollutants, from which estimated permissible concentrations (EPC's) can be derived. Also needed are improved methods for converting toxicological data to the threshold levels represented by EPC's, and biologically supported safety factors for incorporation into the formulae. The complexities of deriving EPC's on the basis of available toxicological data are discussed in Section 5.
- (5) Decision criteria are needed to determine the relative priorities to be assigned to controlling specific pollutants. Compiling and analyzing the data mentioned above will lead to these criteria. Approaches to this somewhat subjective exercise are discussed in Section 6.
- (6) The environmental assessments to be performed as another task on this program will require quantitative emission and distribution data for specific process configurations, coal types, geographic locations, etc. In developing and illustrating assessment criteria and methodologies, this study utilizes approximations of emissions and dilutions such as might be associated with a hypothetical coal cleaning plant.

## 1.2 Potential Environmental Pollutants/Regulations

The pollutants directly associated with coal cleaning are primarily inorganic compounds associated with the ash fraction. Water will be the major receptor of these pollutants; operations causing major emission of air pollutants are infrequent in coal cleaning. The largest air emissions will arise as particulates from thermal dryers and as fugitive dust from coal storage and refuse piles and coal handling. The reverse situation is true in the ultimate combustion of coal; air emissions, particularly SO<sub>2</sub> and suspended particulates, are of much more concern than water effluents.

Lists of potential pollutants from coal cleaning and utilization containing hundreds of entries have been compiled. To arrive at a more manageable number, a "Priority 1" list was selected to include those elements and substances already identified as pollutants of concern, and whose presence in finite concentrations in coal cleaning processes is known or highly suspected. This list contains 49 elements and 23 substances or groups of substances, the latter including such well-known items as SO<sub>2</sub>, total suspended particulates (air), and total suspended solids (water).

An abbreviated pollutant "short list" of eight elements and four compound groups was also employed to limit the scope of some of the exploratory studies undertaken.

Abundance is a factor in evaluating the significance of a pollutant. Almost every naturally occurring element occurs in coal, but the abundances vary widely, both regionally and from seam to seam. Averages and ranges representative of U. S. coals determined by the Illinois Geological Survey are being used in pollutant evaluations.

Health and ecological considerations are important criteria for assessing environmental pollutants. Also important are Federal and state regulations governing emissions. Recent significant changes in Federal regulations have occurred, and more are mandated by laws passed but not yet fully implemented. Some of these will directly affect allowable emissions from coal cleaning processes. Others will affect the processes indirectly, through new and more restrictive regulations governing emissions from coal utilization.

The Clean Air Act Amendments of 1977 may have the most effect on both coal cleaning and utilization. Earlier regulations had established New Source Performance Standards (NSPS) for particulate emissions from coal cleaning plants. The 1977 Amendments require establishing percentage reduction standards for SO<sub>2</sub> emissions from the combustion of coal in large electric utility steam generating units; 85 percent has been proposed. This cannot now be achieved by coal cleaning alone. The effects of these probable regulations on the utilization of coal cleaning is uncertain. More restrictive regulations on existing boilers, which are also possible, may increase the demand for cleaned coal. Existing boilers are likely to represent a larger market for clean coal than new boilers for years to come.

Other sections of the Clean Air Act Amendments of 1977 which may significantly influence both the role of cleaned coal and the operation of coal cleaning plants are those to prevent significant deterioration of air quality (PSD) and the emission control measures which will be required in nonattainment areas not now achieving primary or secondary ambient air quality standards. States are to continue to make "reasonable further progress" in achieving annual incremental reductions of pollutants not meeting standards; these requirements will tend to favor cleaner fuels.

In 1977, effluent guidelines were promulgated for existing coal cleaning plants and proposed for new sources. Regulated pollutants are total suspended solids (TSS), iron, and manganese. Discharge limits for TSS are sufficiently low (35 ppm for a 30-day average) so that any plant in compliance should have no siltation problem downstream. The proposed performance standards for new sources are structured to strongly favor the recycle of wastewater. No discharge of pollutants is permitted for sources which do not recycle wastewater.

The Clean Water Act of 1977 introduced a new requirement for the control of toxic pollutants which are to be limited by the application of the best available technology economically achievable (BATEA). Pursuant to this act, the EPA Administrator published a list of 65 toxic pollutants for which effluent standards are required. Regulations previously existed for six of the listed pollutants, but regulations have not yet been promulgated for any of the other listed pollutants. EPA has further identified specific compounds, within the chemical classes in the published list, to be considered for effluent standards. The thirteen elements in the published list, and their compounds, should receive emphasis in the environmental assessment of coal cleaning processes because of their observed existence in coal. However, none of the classes of organic chemicals in the list appears to have significance as a pollutant from coal cleaning processes because they have not been observed to exist in coal and have not been used as agents in coal cleaning operations.

Existing regulations for solid waste disposal, basically only guidelines, do not establish new standards but set forth requirements and recommended procedures to ensure that the design, construction, and operation provide for environmentally acceptable land disposal site operations. Additionally,

their thrust is toward sanitary and municipal wastes, and mining or coal cleaning wastes are essentially ignored.

The management of solid and hazardous wastes entered a new era on October 21, 1976, upon the passage of the comprehensive Resource Conservation and Recovery Act (RCRA) of 1976. Although the Act has not yet been implemented, it is already clear that the management of solid and hazardous wastes will be revolutionized by the specific regulations now in the process of being drafted by EPA. Whether coal cleaning refuse (and combustion ash) will be classified as hazardous wastes is presently uncertain.

### 1.3 Estimating Environmental Concentrations

Estimates of environmental concentrations of pollutants are needed during the interim period before field measurements of emissions and environmental concentrations can be conducted at actual operating plants. These estimates of environmental concentrations must be based upon pollutant emission rates, which are themselves estimates.

Estimates of emission concentrations are based on process configurations, coal type and composition, percentage recovery, and fractionation factors, among other parameters. All of these parameters except the fractionation factor are controlled or reasonably well-known. Fractionation factors are characteristic of a given coal but vary among coals. In this study, the fractionation factors used were based on the coal washability tests conducted on numerous coals by the Illinois Geological Survey. Illustrative emission calculations use a simple mass-flow model of a coal cleaning plant and fractionation factors appropriate for the assumed coal; simulation experiments were made both with and without assumed pollution controls.

Only limited efforts were directed to physical transport and dispersion models. The state of the art in this area is quite advanced and the principal problem will be in selecting the model or combination of models to use. Air dispersion and dilution models are well known and readily available. Only simple models of dispersion and dilution in surface water courses may be needed, since most streams receiving coal cleaning plant effluents are so small they can possibly be treated as fully mixed. The areas of greatest uncertainty are leaching and runoff of precipitation through coal storage and coal refuse piles and percolation through the bottoms of tailings ponds. Available

simplified approaches to estimating pollutant adsorption and leaching in porous media are expected to be applicable to this general problem.

Ecological transport and distribution previously has been much less well-studied than physical transport and distribution. For this reason, a substantial effort was expended in this study investigating the ecological aspect of the problem. A principal finding of the study is that little is known and much more needs to be learned before predictions can be made with confidence on the ecological transport and fate of potentially hazardous pollutants that might be released by a coal cleaning facility.

The potential sources of coal cleaning pollutants vary from facility to facility but in general include leachate and runoff from coal storage and refuse disposal piles; process wastewater or blowdown from closed water circuits; and dust and gases emitted from coal piles, refuse piles, and thermal dryers. The more apparent environmental effects from these contaminants can be seen in direct contact toxicity resulting from changes in pH in the surrounding media; increasing levels of sulfate sulfur, sulfur dioxide, nitrate nitrogen, and nitrogen oxides; or resultant chemical changes in the abiotic components. These types of effects are usually long term and easily identified. The fate of those trace elements (e.g., arsenic, cadmium, and mercury) whose release is into both terrestrial and aquatic ecosystems is not quite so apparent.

The present preliminary study has focused on the short list of potentially hazardous trace contaminants mentioned previously. These include elemental, inorganic and organic forms of arsenic, beryllium, cadmium, iron, lead, manganese, mercury, and selenium. It is well known and documented that these contaminants are absorbed, retained, released, and cycled among the biotic (i.e., producers, herbivores, omnivores, carnivores, and decomposers) and the abiotic (i.e., soil, groundwater, surface water, and sediment) compartments.

The toxicity of these contaminants to living systems under certain conditions has been established by other researchers. So, the ultimate goal of transport and fate studies is to determine whether or not toxic concentrations could be reached through normal environmental exposure pathways. That is, even if the source release rates for a specific pollutant from a coal cleaning facility were below the current U.S. Government regulations, would concentration of the contaminant ecologically magnify to a point at or beyond the toxic threshold values?



When magnified by an organism, concentration of a contaminant is greater than that of its source or donor compartments. The term describing this is eco-magnification, which is non-source-specific. It includes all potential exposure pathways (ingestion, inhalation, adsorption, and immersion) within the ecosystem. Eco-magnification is frequently misunderstood as a simplistic biological phenomenon when, in fact, it is quite complex. Eco-magnification is all inclusive, whereas the classic term bio-magnification only considers food ingestion as the mode of exposure. Thus, the ability of an organism to accumulate or magnify contaminants depends on a number of ecological, chemical, and physiological factors, such as:

- Chemical form of contaminant
- Concentration of contaminant in soil, water, or air
- Interaction with other trace elements
- Soil characteristics and properties
- Genetic makeup of target organism.

The ultimate goal of the study of ecological transport and fate was to identify likely distribution factors and supply much needed input data for simulation models describing the transport and fate of these pollutants. Computer simulation of transport and fate would enable scientists to compare the computer-predicted long-term body burdens with reported toxic concentrations for individual pollutants. Unfortunately, the need to use computer simulations and then compare the results to reported toxic effects values is ahead of the data base. The data required to accurately calculate the rate transfer coefficients are not available in the literature. Investigators, in general, fail to consider or report: (1) the measurement of major parameters affecting transport and fate, (2) partitioning data into specific exposure sources (i.e., food source, inhalation, direct absorption), (3) chemical form of the pollutant, and/or (4) time duration of the experiment. Therefore, computer modeling to predict ecological transport and fate of pollutants is still beyond the state of the art.

#### 1.4 Developing Environmental Goals

Documenting and evaluating biological effects ideally should precede setting of standards and development of control technology for coal cleaning facilities. The burden of proof of a need for establishing environmental goals

rests with health and ecological effects data; i.e., if no problem exists, there is no need for a solution. Data need to be sound, complete, and rigorous, and they must be interpreted correctly to support environmental goals and recommendations for further development of control devices for coal cleaning facilities. Materials highly toxic to many life stages of many important species during the entire year will require a different level of effort for their control than those mildly toxic to only one unimportant species at a particular time of the year. Unfortunately, the differentiation is not always easy to make. Effects data are not only relatively sparse compared to those needed for adequate assessments but also are typically laboratory results rather than real results from practice. Thus, the following material was developed as another step in providing the necessary feedback for setting standards and for developing control strategies, i.e., which substances need how much control in order to protect health and the environment.

Most biological effects data are obtained in the laboratory and need to be extrapolated to "real world" situations. Extrapolation is the process of inferring or extending a known toxicological response into an unknown area. This extension of knowledge assumes a continuity, similarity, or other parallelism between the two situations. Often biological effects need to be extrapolated from (1) laboratory to field - many differences make this difficult; (2) one species to another - no two species are alike; (3) one medium to another - drinking is not the same as breathing; and (4) one life stage to another - ranges of sensitivity may differ by orders of magnitude. In the present state of the art, biological effects data are collected from a few life stages of a few species for a few routes of entry in a few controlled conditions. On the other hand, the real world situation around a coal cleaning facility contains thousands of species in many stages of growth, all of which may be continuously exposed to various types of doses. Clearly, extrapolation must be done with caution.

Despite the technical difficulties involved in estimating permissible concentrations of toxicants in emission streams, rational approaches are available for dealing with the problem. There are many potentially applicable formulae, some of them developed by or for the U.S. EPA. The formulae have two basic parts: a dose/response part and an adjustments part. The dose/response generally consists of one of the typical laboratory effects measurements:

LD<sub>50</sub>, LC<sub>50</sub>, and TL<sub>m</sub>-96 hr.\* Each effects measurement is adjusted by several factors, the argument being that the adjusted dose/response data better conform to the "real world" situation. Adjustments include the following: media conversion (e.g., airborne to waterborne toxicants), safety factors (e.g., 0.01), various types of exposure (e.g., work day to full week), and elimination rate (biological half-life). All the formulae provide estimates of permissible concentrations for single chemicals. All three media (air, water, and land) are considered for both human and nonhuman populations. The multimedia environmental goals (MEG) chart is the principal tool for displaying these quantitative values and represents a major ongoing work supported by the U.S. EPA. The predicted permissible pollutant concentrations are compared against observed environmental concentrations to identify those pollutants whose concentrations exceed the estimated acceptable level.

Twenty formulae were identified and considered in this study. The formulae were reviewed for their major strengths and limitations from three viewpoints: media, dose/response data, and adjustment factors. This evaluation provided a good basis from which to improve the state of the art.

Ten major strengths of the formulae were identified. Some of the most powerful were embodied in the formulae used to estimate permissible concentrations for airborne pollutants. These formulae use a variety of the most rigorous dose/response data, which include a variety of measurements, e.g., threshold limit values (TLV's) and other large data sets. The ability to incorporate simple adjustment factors is seen as a strength; generally, the prediction is assumed to improve as more adjustment factors are incorporated. Particularly useful adjustment factors are those for exposure time, elimination rates, and safety factors.

Seventeen major limitations of the formulae were identified. From the media viewpoint, the formulae for land- or food-borne pollutants exhibit

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\* LD<sub>50</sub>: Lethal dose 50, i.e., the dose of a pollutant required to kill 50 percent of a particular animal species by methods other than inhalation.

LD<sub>LO</sub>: Lethal dose low, i.e., the lowest dose of a substance introduced in one or more portions by any route other than inhalation over any period of time and reported to have caused death in a particular animal species.

TL<sub>m</sub>: Median threshold limit value, i.e., the concentration in water of a pollutant required to kill 50 percent of a particular aquatic species.

the most limitations; the crop uptake model is too simplistic among other deficiencies. Many available toxicological response data, e.g.,  $LD_{50}$ 's, have not been used in the available formulae. Responses are limited to a few species of animals; few or no responses are provided for plants and microorganisms. The bulk of the effects data are based on acute or short-term exposure when chronic or long-term exposure effects data are needed. The effects data are for single chemicals when responses to mixtures of chemicals are needed. So, from the dose/response viewpoint, there are many deficiencies. From the adjustment factor viewpoint, there is a great need for validation of the reasonableness of the factors. Safety factors need a biological basis. And for every limitation in the effects data, there should be compensatory adjustment. For example, when chronic effects data are not available (the usual case), an adjustment factor can be used with the more readily available acute effects data to estimate chronic effects.

The scope of work permitted research to reduce or remove 5 of the 17 major limitations. The relevance and availability of pertinent data were ranked for each limitation. Five limitations were regarded as the most fruitful research candidates. Their mitigation required research to identify alternative state-of-the-art formulae; correlate nonoral with oral  $LD_{50}$ 's; use chronic effects data; extrapolate data from one species to another; and develop a biological basis for safety factors. The following material summarizes some of the major points achieved in the research.

Other formulae merit incorporation into the present system. Some formulae handle exposure and biological half-lives more rigorously than any one of the twenty formulae. Typical state-of-the-art formulae are those for (1) maximum permissible concentration for radioisotopes, and (2) CUMEX (cumulative exposure) index. Inclusion of the former would provide a more rigorous estimation of waterborne radionuclides and related pollutants. The latter would provide estimates for permissible air and water pollutant exposures separately and simultaneously.

Multiple exposures are the reality, and more formulae capable of handling such exposures need to be developed for future estimations of potential dangers to living organisms.

A major deficiency common to all of these formulae is the inability to utilize the variety of available pertinent toxicological data. For example, one of the best formulae in use requires that dose/response data be in the form

of oral LD<sub>50</sub> for rats. However, there are many nonoral toxicological response data which could be used, if a conversion method were available. To overcome this limitation, specially designed equations have been developed to permit quantitative conversion of toxicological data for nonoral routes of administration to the oral route. Conversions were developed for intravenous, intraperitoneal, and subcutaneous LD<sub>50</sub>'s and inhalation LC<sub>50</sub> to the oral LD<sub>50</sub>. For example, the relationship for intravenous LD<sub>50</sub> to oral LD<sub>50</sub> is:

$$\ln(\text{oral LD}_{50}) = -0.5714 + 1.587 \ln(\text{intravenous LD}_{50}) \quad .$$

This research expands the access to other readily available toxicological effects data and is immediately applicable. However, this research needs to be extended to better utilize the wealth of toxicological data for other routes of administration, e.g., LD<sub>LO</sub>, TD<sub>LO</sub>, LC<sub>LO</sub>, etc., and for other species (e.g., mice, hamsters, and dogs).

Limitations inherent to biological effects data for short-term (acute) exposure can be removed only by use of effects data for long-term (chronic) exposure. Chronic exposure (low levels of chemicals for long periods of time) can depress reproductive capacity, increase the number of malignant tumors, and generally shorten the life span of males, females, or both. Chronic effects for life-term (1000+ days) and multi-generation (three-generation) studies for rodents are discussed herein. Generally, concentrations lower than those used in acute exposure (high levels of chemicals for short periods of time) cause effects that could not have been known on the basis of acute tests only. Concentrations of 5 ppm for some elements in drinking water seem to show increasingly harmful effects the longer the study and the greater the number of generations studied. At present, there seems to be no quantitative way to predict chronic effects based on effects data only from acute experiments. When chronic effects data are available, they should be used in the dose/response part of the formulae if the effects are greater than those indicated by acute exposure data.

Animal toxicity data can be extrapolated from one species to another in two ways. In Method 1, the equation deals with only one toxicant at a time, but this single equation can be used to predict the responses of animals of many sizes (including man) to that particular toxicant. In Method 2, the

equation deals with responses to many different toxicants, but it can only be used to extrapolate from the response of one particular species to the response of another species (say, from rat to human). Both methods are described in detail, using the basic relationship of  $Y = aW^b$  where  $Y$  = the response,  $W$  = body weight (or area), and  $a$  and  $b$  are constants relative to the particular  $Y$ . Examples of both approaches indicate that often the basic data are not readily available. Of the many other limitations with these approaches, not the least is the credibility of even attempting extrapolation of response from one species to another.

The range of sensitivity for certain organisms to given toxicants provides a biological basis for safety factors. Toxic levels and effects of a substance vary greatly. For example, toxicity ratios for young of a species versus adults can vary from 0.002 to 16 - a variation of nearly four orders of magnitude. Green algae species differ in their response to cadmium by a factor of 100. Frog embryos and larvae are more sensitive than adults to mercury by factors of 100 and 1000, respectively. Bird embryos and fetal and newborn mammals are more susceptible to metals than their adult counterparts. Baby mammals appear to be four or five times more sensitive than adults to some chemicals. Thus, in aquatic situations, safety factors of 100 to 1000 seem reasonable if available effects data are from least sensitive (most resistant) species. If effects data are from tests on more sensitive species in an ecosystem, such high safety factors are not needed to protect the less sensitive species. In terrestrial situations, smaller safety factors seem biologically reasonable. For example, 10 to 100 would be reasonable safety factors when the available dose/response data are for resistant species.

All of these improvements still fall short of the needed advancements in this important research to protect human health and the environment from adverse effects. True, the formulae provide quantitative values, and increasingly higher quality effects data and adjustment factors are being used in such formulae. The state-of-the-art predictions are not absolute; they are relative. Furthermore, the relative relationships of one prediction to another may not be correct. Caution is warranted. Validation and future monitoring are needed to confirm the reliability of the predictions. Another major step forward involves the issue of mixtures as compared to single chemical species. The approach of predicting permissible concentrations for single chemical species will need to be replaced by approaches addressing synergistic/

antagonistic effects associated with actual emission streams. Then, the feedback to standards setting and control technology development will be more sound biologically.

### 1.5 Decision Criteria for Prioritization

Since all pollutants from coal cleaning processes are not equal in toxicities nor in quantities, there are differing degrees of hazard, and corresponding differences in the relative importance necessary to be placed upon identifying and controlling them.

All of the parameters making up the total hazard of a pollutant are embodied in the estimated permissible concentration (EPC). However, as noted in the previous section, for many pollutants of known importance, EPC's cannot yet be established.

EPA contractors are developing multimedia environmental goals (MEG) and minimum acute toxicity effluent (MATE) values for an increasing list of pollutants; when this work is complete, a rigorous prioritization of pollutants should be possible--at least into groups of similar hazard. However, because these lists are incomplete, their usefulness is limited.

For the near term, it appears that less rigorous and more pragmatic prioritization criteria may be required to fill the gap. Since the relative importance of controlling a pollutant can be generally assessed from its acute toxicity and its abundance in coal cleaning processes, criteria are available for their categorization. Also, substances with established criteria or those designated as pollutants should be prioritized. The "Priority 1" pollutants mentioned above were selected using criteria of this type.

A further modifying parameter, for which data are not yet available to implement, is the availability or lack of availability of adequate control technology for pollutants identified as inherently high-risk.

### 1.6 Recommendations for Future Work

While substantial progress in developing environmental assessment criteria for coal cleaning processes has been made during the past two years, additional work is required. Recommended tasks include:

- Pragmatically group the Priority 1 pollutants into 3 to 5 severity classes using available data on pollutants from coal cleaning processes (i.e., abundances in raw coal, toxicities, and quantities released). This approach will allow environmental assessments to proceed until data to support more rigorous rankings are available.
- Select, exercise, and validate models recommended to assess physical transport and dilution.
- Determine the relative importance of each ecological exposure pathway; determine the rate transfer coefficients for each dominant pathway; and develop and validate simulation models for ecological transport and fate.
- Continue development of the methodology for establishing realistic environmental goals from the multiplicity of toxicological and epidemiological data which are available; further develop interconversion factors between different routes of administration and between different species; and continue the rationalization of safety factors.

Research needs and recommendations for future work are described in detail in Section 7.



## 2.0 INTRODUCTION

Coal cleaning is one of several energy technologies whose environmental implications are being investigated by the Energy Assessment and Control Division of the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. A primary objective of these environmental assessment programs is to identify potential environmental problems which are likely to be associated with the large-scale commercial application of the technology and to identify suitable mitigative and control measures. Such an approach, when effectively implemented, can eliminate the necessity of subsequent cumbersome and expensive retrofits for pollution control.

The cleaning of coal by removal of noncoal materials is an old art; in its early days it was sometimes no more sophisticated than picking shale and rock from a belt carrying the lump coal. Over the years it has become a much more complex and sophisticated operation, impelled by various economic, technical, and political factors.

Two of the most significant factors have been the sharp increases in the price of coal over the past few years and the increasingly restrictive regulations on emissions of sulfur dioxide. Additionally, the impending substitution of increasing amounts of coal for gaseous and liquid fossil fuels will demand enormous new tonnages of coal. These demands cannot be wholly satisfied by using only the best coals; it will be necessary to rely increasingly upon lower grade coals.

Thus, coal cleaning, which is already an important link in the utilization of coal, especially of the lower grades, will become increasingly important. Cleaning upgrades coal by removing both ash and SO<sub>2</sub>-forming constituents. This reduces pollution from the combustion of coal, at the potential expense of environmental pollution caused by the cleaning operation. Accordingly, both economic and environmental benefits and costs associated with the cleaning process need to be identified and assessed for decision-

making purposes. The benefits and costs can be markedly influenced by the quantities and characteristics of the pollutants emitted, as well as by the type and extent of control technologies needed for control of these pollutants. Both benefits and costs increase as broader and more rigorous controls are introduced. In order to make critical benefit/cost judgments, criteria are needed for rating the relative importance which should be placed on identifying and controlling specific pollutants.

The problems are several. Almost every naturally occurring element is found in coal at some detectable concentration. However, the coal industry heretofore has been so result-oriented and so marginally profitable that it was never possible to generate the needed research data base on pollutant emissions from coal cleaning processes. On the other side of the equation, a similar data gap exists with respect to environmental effects, so that it is not yet known which pollutants should be most controlled or how much control is required. The present investigation is designed to help answer some of these questions.

## 2.1 Basis for Environmental Assessment

The fundamental criterion for evaluating the importance of any pollutant is the relationship between its expected environmental concentration and the maximum concentration which presents no hazard to man or biota on a continuous long-term basis. This threshold concentration is designated as the estimated permissible concentration (EPC).

While simply stated, this concept represents a rather complex utilization of a number of subcriteria dealing with specific phases of the overall problem:

- Selecting those environmental pollutants of most concern
- Selecting methods for estimating environmental concentrations of pollutants resulting from coal cleaning
- Selecting methods for evaluating the EPC's for man and biota.

## 2.2 Approach to Environmental Assessment

The pollutants selected for consideration include those which have already been identified as pollutants of concern and whose presence in coal cleaning processes is known or highly suspected. Such a list is large, and further selection is needed to derive a list with a manageable number of candidates. Substances already identified and designated by EPA as pollutants are almost automatic candidates for consideration.

The criteria for selecting methods for estimating environmental concentrations of pollutants are relatively straightforward. Numerous models have been developed for estimating air and water concentrations resulting from emissions from point sources and for transport and diffusion through the physical environment. Thus, the problem is to select the most suitable model or combination of models.

The basic criterion for an EPC of a potentially hazardous pollutant is that this concentration shall not adversely affect man or biota upon continuous long-term exposure. These are, thus, threshold concentrations, even lower than the TLV's (threshold limit values) suitable for workroom atmospheres. Unfortunately, very few dose/response data at threshold concentrations are available for the pollutants of concern in coal cleaning processes. Available data are, characteristically, for acute or chronic exposures, and hardly ever for man. Conversion of such data to EPC's poses some major problems, which have not yet been totally overcome. More work in this area is badly needed.

### 3.0 POTENTIAL ENVIRONMENTAL POLLUTANTS AND APPLICABLE REGULATIONS

The extent of the universe of potential pollutants for this study depends on the boundaries adopted for coal cleaning processes. The definition of these boundaries has evolved during the conduct of this study. Initially, the universe was taken to include pollutants generated during the combustion of coal in coal-fired power plants and the burning of coal refuse piles. Under this interpretation, the myriad organics formed by the combustion of coal in oxygen-deficient regimes (coking-type reactions) were included as representative of gob-pile burning. These numbered in the hundreds; over 800 compounds have been identified from the coking of coal. Many different pollutants have been identified as being associated with raw coal or with some segment of the coal industry. A number of lists from various sources, containing hundreds of elements and compounds, have been compiled and were presented in Battelle's coal cleaning technology overview draft report.<sup>(1)</sup>

As a result of discussions with the U.S. EPA Project Officer, the scope of this subtask was subsequently redefined to include (1) only those activities directly related to coal cleaning, handling, transportation, and storage, and (2) a Priority 1 list of potential pollutants, discussed later, which contains 74 of the principal pollutants of concern.

#### 3.1 Universe of Pollutants

##### 3.1.1 Pollutants of Concern

The original lists of potential pollutants, reproduced in the technology overview draft report<sup>(1)</sup> were based on a survey of other experimental investigations. These studies had been performed by different investigators with different objectives and different approaches, so that there are major differences in the manner and format in which the results are presented. In some

cases, the approach was mineralogical, i.e., individual minerals and mineral classes were identified. In others, where wet chemical analyses were performed, pollutants were variously reported as oxides, in some other analytical convention, or, often, on an elemental basis. Trace element analysis results, by either emission spectrography or spark source mass spectrography (SSMS), report only the element, giving no indication of the chemical form(s) present.

Thus, one of the first tasks involved the reorganization and rationalization of the overlapping lists, particularly the organic compounds. However, even after the rationalization of the list of organic compounds, many hundreds remained, only a fraction of which could be represented by "type" compounds representative of the numerous subgroups. Reexamination of the basic problem led to the conclusion that the boundaries could and should be narrowed, to eliminate pollutants that result from coking-type reactions. Most of these compounds will be present in only minute quantities, some not at all, in oxidizing combustion gases, such as are encountered in thermal coal dryers or in coal-fired power plants.

Gob-pile burning is not an intrinsic operation in coal cleaning; rather, it is symptomatic of mismanagement of refuse piles. The simple solution, which eliminates a need to consider the related complex organic compounds, is prevention of such burning.

The pollutants directly associated with the cleaning of coal are primarily inorganic compounds associated with the ash fraction. Water will be the principal receptor of these pollutants. Operations causing major emissions of air pollutants are infrequent in the cleaning of coal. The largest air emissions will include fugitive dust from coal handling and transfers, and particulates and combustion products from thermal dryers.

As the investigation progressed, it became clear that it would be advantageous to develop a relatively small list of pollutants of most interest for the first-phase effort. The original goal was a list of 50 or less; as the list was created, it seemed advisable to slightly exceed this number, and the final list contains 74 entries.

For the first phase, a logical criterion for selection was to define Priority 1 pollutants as those that already have been identified as pollutants of concern and whose presence in finite concentrations in coal cleaning processes is known or suspected. The chemical substances on this list were

drawn from a number of sources, including:

- EPA criteria pollutants for air<sup>(2,3)</sup>
- Pollutants identified by effluent guidelines for coal mining and coal preparation<sup>(4,5)</sup>
- Substances included in EPA "Quality Criteria for Water"<sup>(6)</sup>
- Toxic and hazardous pollutants listed by EPA which may be associated with coal cleaning.<sup>(7,8)</sup>

In addition to these specific pollutants, a number of more general non-chemical pollutants and aggregated pollutant parameters were included in the list. The proposed list, shown in Table 3-1, includes 51 elements and 23 chemical substances or aggregated pollutant parameters. The selection of elements was based on a number of factors, including their recognition by EPA as pollutants to be regulated, their elemental group, their abundance in coal, and the availability of information on toxicity, abundance, fractionation factors, etc.

The elements selected and their relationship to the rest of those in the periodic table are shown in Figure 3-1; the omitted elements are shaded. The following elemental groups, or portions thereof, were omitted for the reasons shown:

- |   |                                   |
|---|-----------------------------------|
| ● Hydrogen  | Not applicable                    |
| ● Group IIIB, except lanthanum which will represent the group                               | Low abundance; low toxicity       |
| ● Group VIIIA, fixed gases  | Not applicable                    |
| ● Group VIII, all precious metals   | Low abundance; low toxicity       |
| ● All lanthanides, except lanthanum   | Low abundance; low toxicity       |
| ● All actinides, except uranium and thorium   | Not applicable                    |
| ● All other radioactive elements, i.e., technetium, radium                                  | Not applicable; low abundance     |
| ● All elements above atomic number 57, except mercury, thallium, lead, uranium, and thorium | Low abundance; little information |

While the selection rules may be somewhat arbitrary, the elements selected are judged to include those of greatest priority. Other elements and substances not listed should not be considered as nonhazardous but as falling in a lower

TABLE 3-1. PROPOSED PRIORITY 1 POLLUTANTS FOR COAL CLEANING PROCESSES

Elements	Specific Pollutant Limitations <sup>(a)</sup>								Elements	Specific Pollutant Limitations <sup>(a)</sup>							
	A	B	C	D	E	F	G	H		A	B	C	D	E	F	G	H
Aluminum									Magnesium								
Antimony		X					X		Manganese		X			X			X
Arsenic		X			X		X	X	Mercury			X		X	X	X	X
Barium		X			X			X	Molybdenum		X						
Beryllium			X				X	X	Nickel		X					X	X
Boron		X						X	Niobium								
Bromine		X							Nitrogen								
Cadmium					X	X	X	X	Oxygen								
Calcium		X							Phosphorus								X
Carbon									Potassium								
Cerium									Rubidium								
Cesium									Selenium					X		X	X
Chlorine		X <sup>(b)</sup>						X	Silicon								
Chromium		X <sup>(b)</sup>			X		X	X	Silver							X	
Cobalt		X <sup>(b)</sup>							Sodium								
Copper		X <sup>(b)</sup>					X	X	Strontium								
Fluorine		X							Sulfur								
Gallium									Tellurium		X						
Germanium									Thallium							X	
Indium									Thorium								
Iodine		X							Tin								
Iron					X			X	Titanium		X						
Lanthanum									Uranium		X						
Lead					X		X	X	Vanadium		X						
Lithium									Zinc		X			X		X	X

TABLE 3-1. (Continued)

Specific Pollutant Limitations <sup>(a)</sup>										Specific Pollutant Limitations <sup>(a)</sup>									
Elements	A	B	C	D	E	F	G	H		Elements	A	B	C	D	E	F	G	H	
Zirconium	X									Organic Nitrogen Compounds									
<u>Groupings</u>										Polycyclic Organic Materials (POM's)									
Alkalinity								X		Carbon Chloroform Extract (CCE)					X				
Ammonia	X							X											
Cyanide	X			X	X	X	X	X											
Chlorides				X															
Nitrates				X				X											
Sulfides																			
Sulfates					X														
SO <sub>x</sub>	X	X																	
NO <sub>x</sub>	X	X																	
Total Suspended Solids (TSS)																			
Total Dissolved Solids (TDS)					X														
Chemical Oxygen Demand (COD)																			
Total Suspended Partic. (TSP)	X			X															
Carbon Dioxide	X																		
Carbon Monoxide	X	X																	
Hydrocarbons	X																		
Photochemical Oxidants	X																		
Oil and Grease								X											
Phenols	X			X				X											
Organic Sulfur Compounds																			

(a) Column headings are defined as follows:

- A. National Primary and Secondary Ambient Air Quality Standards<sup>(2)</sup>
- B. OSHA Standards for Workroom Air Contaminants<sup>(9)</sup>
- C. National Emission Standards for Hazardous Air Pollutants<sup>(7)</sup>
- D. New Stationary Source Performance Standards (Coal Preparation Plants)<sup>(4)</sup>
- E. Interim Drinking Water Regulations (EPA)<sup>(10)</sup>
- F. EPA Toxic Pollutant Effluent Standards (Proposed)<sup>(11)</sup>
- G. EPA Toxic Pollutant List<sup>(8)</sup> (See Table 3-8)
- H. EPA Water Quality Criteria (Proposed - not regulations)<sup>(6)</sup>

(b) Metal as fume or dust.





priority class. Also, some of the 51 elements now included may be dropped later on the basis of insignificant abundance or lack of sufficient information for analysis and evaluation.

The remaining 23 entries on the proposed Priority 1 list comprise a number of substances (e.g., sulfur dioxide) defined statutorily as a criteria air pollutant, as well as aggregated pollutant parameters (e.g., total suspended solids), also defined as a pollutant in effluent guidelines.<sup>(5)</sup> Since many pollutants of the latter type may be found in variable and undefinable mixtures, there may be insufficient information to permit their treatment in a rigorous fashion.

Table 3-1 also indicates where existing and proposed standards and criteria are judged to have application to coal cleaning processes, based in part on Cleland and Kingsbury's recent draft report of key Federal regulations.<sup>(12)</sup> Column H indicates water quality criteria recently issued by EPA<sup>(6)</sup> which will achieve the status of regulations when they are ultimately adopted by the states as part of their implementation plans. Column G in Table 3-1 lists the elements included in the recent "Toxic Pollutant List" published by EPA.<sup>(8)</sup>

Although the Priority 1 list satisfies the requirement of a manageable list containing the important pollutants expected from coal cleaning processes, there appeared to be a need for an even more abbreviated list suitable for preliminary testing of some of the concepts and approaches to environmental assessment. To meet this need, an abbreviated "short list" has been proposed which includes the following chemical pollutants:

Arsenic	Manganese
Beryllium	Selenium
Cadmium	Sulfate sulfur
Iron	Sulfur dioxide
Mercury	Nitrate nitrogen
Lead	Nitrogen oxides

This list, which includes both air and water pollutants, is suitable for the evaluation of chemical and physical transport models, as well as estimated emissions and permissible concentrations.

When the data base on Priority 1 pollutants is complete, it is recommended that a Priority 2 list of pollutants be selected for further consideration. Such pollutants, by definition, would be of lesser importance and concern, on

the basis of today's knowledge of estimated environmental concentrations and estimated permissible concentrations. Such a list may include part or all of the pollutants initially identified as being in the universe of potential pollutants.

Compilation and analysis of data on the Priority 2 pollutants probably will result in the upgrading of a few to the lower end of the Priority 1 group, with the rest assigned to the category of less important pollutants.

### 3.1.2 Pollutants in Coals

The importance of a pollutant is a function not only of its toxicity but also of its abundance. Thus, the quantities of the pollutants cited above in coal are an important parameter. Unfortunately, there is no simple measure of abundance; the composition of coals varies greatly, not only from region to region, but also from seam to seam and within a seam. Thus, analysis and comparison demand recourse to averages and ranges about those averages. Probably the most complete and definitive investigation of the analyses of coals has been the work of Ruch, Gluskoter, et al., at the Illinois State Geological Survey.<sup>(13,14)</sup> This group has analyzed, in considerable detail, hundreds of U.S. coal samples, not only from the Illinois Basin, but elsewhere. Summaries of their analyses of 165 coal samples from three regions are presented in Table 3-2. It is apparent that the concentrations of some pollutants range tremendously, from sample to sample. The inclusion of a few exceptionally high values will severely bias an arithmetic mean. Thus, although both arithmetic and geometric means were reported, geometric means are regarded as better measures of the central value and are shown here. Also, as pointed out by Gluskoter, et al.,<sup>(14)</sup> the geometric mean more closely approximates the value that would be expected in an unknown sample.

The geometric mean concentrations listed in Table 3-3 for the eight elements on the Priority 1 "short list" are illustrative. Even though there are fairly large variations, the order of magnitude is consistent, suggesting that these averages are suitable for generic, non-site-specific environmental assessments.

TABLE 3-2. MEAN ANALYTICAL VALUES FOR ELEMENTAL CONCENTRATION IN COAL SAMPLES FROM VARIOUS REGIONS<sup>(14)</sup>

Element	Illinois Basin <sup>(a)</sup>			Appalachian Coals <sup>(b)</sup>			Western Coals <sup>(c)</sup>		
	Geometric Mean, ppm	Range, ppm		Geometric Mean, ppm	Range, ppm		Geometric Mean, ppm	Range, ppm	
		Minimum	Maximum		Minimum	Maximum		Minimum	Maximum
Aluminum	12,000	4,300	30,000	16,000	11,000	31,000	8,800	3,100	22,000
Antimony	0.81	0.1	8.9	1.1	0.25	7.7	0.45	0.18	3.5
Arsenic	7.4	1.0	120	15	1.8	100	1.5	0.34	9.8
Barium	75	5.0	750	170	72	420	450	160	1,600
Beryllium	1.6	0.5	4.0	1.1	0.23	2.6	0.35	0.10	1.4
Boron	98	12	230	28	5.0	120	48	16	140
Bromine	10	0.6	52	8.9	0.71	26	2.1	0.5	25
Cadmium	0.6	0.1	65	0.19	0.10	0.6	0.15	0.10	0.60
Calcium	5,100	100	27,000	3,400	900	26,000	15,000	440	38,000
Cerium	12	4.4	46	23	11	42	9.1	2.8	30
Cesium	1.2	0.5	3.6	1.6	0.4	6.2	0.16	0.02	3.8
Chlorine	800	100	5,400	1,000	100	8,000	200	100	1,300
Chromium	16	4.0	60	18	16	90	8.1	2.4	20
Cobalt	6.0	2.0	34	7.6	1.5	33	1.5	0.6	7
Copper	13	5.0	44	16	5.1	30	8.5	3.1	23
Dysprosium	1.0	0.5	3.3	2.0	0.7	3.5	0.57	0.22	1.4
Europium	0.25	0.1	0.9	0.47	0.16	0.9	0.16	0.07	0.80
Fluorine	63	29	140	84	50	150	57	19	140
Gallium	3.0	0.8	10	5.2	2.9	11	2.1	0.8	6.5
Germanium	4.8	1.0	43	0.87	0.1	6	0.5	0.10	3.0
Hafnium	0.49	0.13	1.5	1.1	0.6	2.2	0.7	0.26	1.3
Indium	0.13	0.01	0.43	0.22	0.13	0.37	0.07	0.01	0.25
Iodine	1.2	0.24	14	1.4	0.33	4.9	0.46	0.20	1.0
Iron	19,000	4,500	41,000	13,000	500	26,000	4,900	3,000	12,000
Lanthanum	6.4	2.7	20	14	6.1	23	4.5	1.8	13
Lead	15	0.8	220	4.7	1.0	18	2.6	0.7	9.0
Lutetium	0.08	0.02	0.44	0.18	0.04	40	0.05	0.01	0.43
Magnesium	500	100	1,700	500	200	1,500	1,200	300	3,900
Manganese	40	6.0	210	12	2.4	61	28	1.4	220
Mercury	0.16	0.03	1.6	0.17	0.05	0.47	0.07	0.02	0.63
Molybdenum	6.2	0.3	29	1.8	0.10	22	0.59	0.10	30
Nickel	19.	7.6	68	14	6.3	28	4.4	1.5	18
Phosphorus	45	10	340	81	15	1,500	82	10	510
Potassium				21.80			300	100	3,200
Rubidium	17	2.0	46	19	9.0	63	2.4	0.3	29
Samarium	1.1	0.4	3.8	2.4	0.9	4.3	0.56	0.22	1.4
Scandium	2.5	1.2	7.7	4.5	1.6	9.3	1.5	0.50	4.5
Selenium	2.0	0.4	7.7	3.4	1.1	8.1	1.3	0.40	2.7
Silicon	23,000	5,800	47,000	26,000	10,000	63,000	13,000	3,800	47,000
Silver	0.03	0.02	0.08	0.02	0.01	0.06	0.02	0.01	0.07

TABLE 3-2. (Continued)

Element	Illinois Basin (a)			Appalachian Coals (b)			Western Coals (c)		
	Geometric	Range, ppm		Geometric	Range, ppm		Geometric	Range, ppm	
	Mean, ppm	Minimum	Maximum	Mean, ppm	Minimum	Maximum	Mean, pp	Minimum	Maximum
Sodium	300	-	2,000	300	100	800	600	100	600
Strontium	30	10	130	100	28	550	220	93	500
Sulfur	34,000	5,600	64,000	19,000	5,500	50,000	7,000	3,400	19,000
Tantalum	0.14	0.07	0.3	0.26	0.12	1.1	0.12	0.04	0.33
Terbium	0.18	0.04	0.65	0.28	0.06	0.63	0.17	0.06	0.58
Thallium	0.59	0.12	1.3	-	-	-	-	-	-
Thorium	1.9	0.71	5.1	4.0	1.8	9.0	1.8	0.62	5.7
Tin	0.94	0.2	51	0.97	0.2	8.0	0.43	0.10	15
Titanium	600	200	1,500	900	500	1,600	500	200	1,300
Tungsten	0.63	0.04	4.2	0.62	0.22	1.2	0.58	0.13	3.3
Uranium	1.3	0.31	4.6	1.3	0.40	2.9	0.99	0.30	2.5
Vanadium	2.9	11	90	35	14	73	12	4.8	43
Ytterbium	0.53	0.27	1.5	0.73	0.18	1.4	0.34	0.13	0.78
Zinc	87	10	5,300	19	2.0	120	5.0	0.30	17
Zirconium	41	12	130	41	8.0	88	26	12	170

(a) 114 Samples

(b) 23 Samples

(c) 28 Samples.

TABLE 3-3. GEOMETRIC MEAN CONCENTRATIONS OF EIGHT ELEMENTS IN COAL<sup>(14)</sup>

	Concentration, ppm		
	Illinois Basin	Appalachian	Western
Arsenic	7.4	15	1.5
Beryllium	1.6	1.1	0.35
Cadmium	0.6	0.19	0.15
Iron	19,000	13,000	4900
Lead	15	4.7	26
Manganese	40	12	28
Mercury	0.16	0.17	0.07
Selenium	2.0	3.4	1.3

Another factor needing consideration, however, is the fact that coal dust appears to be significantly enriched in inorganic constituents compared to coal, as suggested by Blackwood and Wachter.<sup>(15)</sup> They compared the analysis (by spark source mass spectrometry) of a "typical" coal with that of particulate matter from personal samplers carried by coal miners, considered to represent the dust in the interior of a mine. It is assumed that the samples were from comparable coals, although this is not explicitly stated in the original report.<sup>(16)</sup> As shown by Table 3-4, the concentrations of almost all elements were greater in the respirable dust fractions than in coal, in some instances by large factors.

### 3.2 Federal and State Standards and Criteria

One aspect of this study was a summarization of Federal and state regulations governing pollution resulting from activities associated with coal cleaning, transportation, storage, and handling. This scope, as defined, was considered to include the combustion of coal as a fuel, but not the conversion of coal to coke or other liquid or gaseous fuels. Also, the investigation focused on pollution, per se, and hence excluded other regulations which may impinge upon coal cleaning processes, such as those governing health and safety standards for the work place environment or the quality of community drinking water supplies. Some of these other regulations are discussed in several recent reports.<sup>(12,17)</sup>

Pollution regulations with direct influence on coal cleaning activities were discussed in an earlier preliminary report on the development of environ-

TABLE 3-4. CONCENTRATIONS OF TRACE METALS IN  
COAL AND COAL DUST(15)

Element	Concentration, ppm		Element	Concentration, ppm	
	Coal	Coal Dust		Coal	Coal Dust
Aluminum	Major	283,000	Sodium	5,000	755
Arsenic	0.30	26.4	Strontium	100	291
Barium	69	453	Sulfur	6,100	3,130
Bismuth	0.20	7.50	Tellurium	0.25	3.80
Bromine	0.30	11.3	Titanium	620	15,800
Boron	42	3.80	Uranium	1.9	2.26
Cadmium	0.19	3.80	Vanadium	12	166
Calcium	4,000	13,200	Yttrium	7.7	7.60
Cerium	13	45.3	Zinc	10	415
Chlorine	130	230	Zirconium	76	60.4
Chromium	4.5	170			
Cobalt	2.3	11.3			
Copper	25	868			
Fluorine	5.7	1.90			
Gallium	8.7	68.0			
Germanium	0.33	18.9			
Iodine	0.20	3.80			
Iron	1,600	79,200			
Lanthanum	5.8	22.6			
Lead	3.9	26.4			
Magnesium	4,500	792			
Manganese	30	45.3			
Molybdenum	3.0	15.1			
Neodymium	8.3	45.3			
Nickel	2.7	755			
Niobium	20	7.60			
Phosphorus	380	306			
Potassium	410	16,600			
Praseodymium	4.7	11.1			
Rubidium	3.0	7.60			
Samarium	1.7	3.80			
Scandium	1.3	30.2			
Selenium	0.32	7.60			
Silicon	Major	294,000			
Silver	0.22	7.60			

mental assessment criteria,<sup>(18)</sup> which was subsequently updated.<sup>(19)</sup> However, pollution regulations frequently change, and both of the above summaries are already out of date. By the same token, pending and foreseeable developments further regulating pollution will probably make portions of the following discussion obsolete within the next six months to a year.

The following Federal Acts constitute the primary regulatory authority governing pollution from activities associated with coal cleaning processes.

Air Pollution

Clean Air Act of 1970	(P.L. 91-604)
Energy Supply and Environmental Coordination Act of 1974	(P.L. 93-319)
Clean Air Act Amendments of 1977	(P.L. 95-95)

Water Pollution

Federal Water Pollution Control Act Amendments of 1972	(P.L. 92-500)
Clean Water Act of 1977	(P.L. 95-217)

Solid Waste

Solid Waste Disposal Act of 1965	(P.L. 89-272)
Resource Recovery Act of 1970	(P.L. 91-512)
Resource Conservation and Recovery Act of 1976	(P.L. 94-580)

All of the above Acts are administered and enforced by the U.S. Environmental Protection Agency and are embodied in Title 40 of the Code of Federal Regulations.

The applicability of the provisions of these Acts to coal cleaning will be discussed in the following sections. The discussion will not include other Federal Acts which at this time are only potentially applicable. For instance, the Toxic Substances Control Act (P.L. 94-469), enacted in 1976, instructs the EPA Administrator to use other Federal laws to protect against the risks of toxic substances, unless it is in the public interest to use TSCA. While the possibility exists of adopting this alternative to control coal cleaning pollutants classified as toxic substances, it is regarded as slight.



The discussion will also contain some general mention of state pollution regulations. State regulations are generally written or amended to incorporate, as a minimum, the provisions of the Federal laws. In some instances, state regulations are more stringent than are the Federal regulations. The states are usually required to submit implementation plans for EPA approval outlining how Federal standards will be met and specifying a reasonable time frame for implementing those standards. This state certification procedure is essentially complete for air pollution, well underway for water pollution, and just beginning for solid wastes.

### 3.2.1 Air Pollution Regulations

3.2.1.1 Federal. The development and implementation of air pollution controls has been approached in two different ways by the U.S. Environmental Protection Agency, in accordance with the provisions of the Clean Air Act. Emission standards regulate the quantities of pollutants emitted from sources; ambient air quality standards regulate the concentrations of pollutants in the atmosphere.

3.2.1.1.1 Ambient Air Quality Standards. The U.S. EPA, under Section 109 of the Clean Air Act, has established national primary and secondary ambient air quality standards (NAAQS), which regulate pollutant levels in order to protect, respectively, human health and public welfare (property and plant and animal life).<sup>(2)</sup>

Implementation is the responsibility of the individual states, under a State Implementation Plan (SIP) which must be approved by EPA. Also, the permissible levels for certain named pollutants (criteria pollutants) are established by EPA and must not be exceeded in the SIP. Some of these "criteria pollutants" arise mainly from motor vehicles. Those of interest to coal cleaning processes (total suspended particulates, sulfur oxides, and nitrogen oxides) arise from stationary sources and are generated mainly from coal combustion. Current national ambient air quality standards for the criteria pollutants are summarized in Table 3-5.

A national ambient air quality standard for lead has just been promulgated.<sup>(3)</sup>

TABLE 3-5. NATIONAL AMBIENT AIR QUALITY STANDARDS (2)

		Permissible Concentration, $\mu\text{g}/\text{m}^3$ (ppm)	
		Primary	Secondary
Averaging Period			
<u>Particulates</u>	Annual Geometric mean	75	60
	Max. 24-hr concentration, not to be exceeded more than once per year	260	150
<u>Sulfur dioxide</u>	Annual arithmetic mean	80 (0.03)	60 (0.02)
	Max. 24-hr concentration, not to be exceeded more than once per year	365 (0.14)	260 (0.1)
	Max. 3-hr concentration, not to be exceeded more than once per year	--	1300 (0.5)
<u>Carbon monoxide</u>	Max. 8-hr concentration, not to be exceeded more than once per year	10 (9)	10 (9)
	Max. 1-hr concentration, not to be exceeded more than once per year	40 (35)	40 (35)
<u>Hydrocarbons</u>	Max. 3-hr (6-9 a.m.) concentration, not to be exceeded more than once per year	160 (0.24)	160 (0.24)
<u>Photochemical oxidants</u>	Annual arithmetic mean	--	--
	Max. 4-hr concentration	--	--
	Max. 1-hr concentration, not to be exceeded more than once per year	160 (0.08)	160 (0.08)
<u>Nitrogen dioxide</u>	Annual arithmetic mean	100 (0.05)	100 (0.05)

This is designed to regulate emissions from the nonferrous metals industry and the combustion of leaded gasoline and will have no effect upon coal cleaning processes.

3.2.1.1.2 New Source Performance Standards. In accordance with Section III of the Clean Air Act, EPA is required to compile a list of categories of emission sources that may contribute significantly to air pollution and to establish Federal standards of performance for new and modified stationary sources in such categories. Unlike the ambient air quality standards, these standards of performance are not based on the effects of pollutants on public health and welfare, but on "the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated."\* Agency terminology for this is Best Available Control Technology (BACT).

Regulations have now been promulgated for over 25 types of sources. The foremost category on the list is fossil-fuel-fired stationary sources; many provisions of the Clean Air Act Amendments of 1977 are aimed specifically at such sources, and the restrictions applied are much more rigorous than in the past. Where the original New Source Performance Standard (NSPS) for large (>250 million Btu/hr heat input), coal-fired boilers permitted the emission of 1.2 lb SO<sub>2</sub>/million Btu, the 1977 Amendments specify, in addition, that the revised NSPS "...shall reflect the degree of emission limitation and the percentage reduction achievable through application of the best technological system of continuous emission reduction...", i.e., a percentage reduction will be required rather than maintenance of emissions below an upper limit. The criteria are tempered by the usual energy, cost, and environmental impact considerations. Also, credit may be taken for any cleaning of the fuel or reduction in the pollution characteristics of the fuel after extraction and before combustion.

The 1977 Amendments require the promulgation of regulations not later than one year after the date of enactment, i.e., by August 7, 1978. However, framing of the regulations is behind schedule. Proposed regulations

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\* It should be noted that the setting of NAAQS provides the justification for setting emission standards for these pollutants.

were published for comment on September 19, 1978.<sup>(20)</sup> The proposed standards for solid fuels would continue to limit maximum SO<sub>2</sub> emissions to 1.2 lb/million Btu, and, additionally, uncontrolled SO<sub>2</sub> emissions would be required to be reduced by 85 percent (on a daily basis). For three days per month a 75 percent reduction requirement would apply, providing some allowance for system variance.

A key provision in the proposed SO<sub>2</sub> standards is that exemptions would not be allowed for malfunctions. Suggested compliance alternatives include installation of spare FGD modules, derating of steam generators, or temporary shutdown and satisfaction of electric demand from other sources.

The proposed particulate emission standard would be reduced from the present 0.1 lb/million Btu to 0.03 lb/million Btu, and uncontrolled particulate matter emissions would have to be reduced by 99 percent. These proposed emission standards are based on emission levels achievable with electrostatic precipitators (ESP) and baghouses.

Proposed NO<sub>x</sub> emission standards for bituminous coals are decreased to 0.6 lb/million Btu from the present 0.7 lb limit, with the additional requirement of a 65 percent reduction from uncontrolled emissions, although the percent reduction would not be controlling.

Since the proposed NSPS apply only to electric utility steam generating units larger than 250 million Btu/hr heat input, no boilers employed in coal cleaning activities will be affected by these new standards. On the other hand, many, if not most, of the utility users of coal use boilers of this size or larger. Thus, depending somewhat on the SO<sub>2</sub> regulations finally promulgated, the revisions to the NSPS for fossil fuel boilers are likely to have a significant, but indirect, impact upon coal cleaning. The role of coal cleaning in the utilization of coal undoubtedly will be influenced materially, although in what way is as yet unclear. The percentage reductions required are unlikely to be achievable by coal cleaning alone, so that some supplemental form of SO<sub>2</sub> removal probably will be required. On the other hand, the converse may also be true, especially on high-sulfur coals, so that coal cleaning may be technically desirable (and possibly also economically advantageous) to supplement flue gas desulfurization. Additionally, coal cleaning offers a non-capital-intensive option for significantly reducing SO<sub>2</sub> emissions from the generally smaller industrial boilers, for which emission regulations have not yet been proposed.

New source performance standards which are directly applicable to coal cleaning processes are those for new and modified coal preparation plants and handling facilities. Processes covered include thermal dryers, pneumatic coal cleaning equipment (air tables), coal processing and conveying equipment (including breakers and crushers), coal storage systems (except for open storage piles) and coal transfer and loading systems (including barge loading facilities). [Although the regulations in 40 CFR Part 60.250<sup>(4)</sup> do not specify their application other than to coal preparation plants, the explanatory discussion in the promulgation announcement (41 Federal Register 2232, January 15, 1976) also included other sources which handle large amounts of coal, such as power plants, coke ovens, etc.]

Limitations set by these NSPS, applicable to all coal preparation or handling facilities processing more than 200 tons/day, include:

- Emissions from thermal dryers may not exceed 0.070 g/dscm (0.031 gr/dscf) and 20 percent opacity.
- Emissions from pneumatic coal cleaning equipment may not exceed 0.040 g/dscm (0.018 gr/dscf) and 10 percent opacity.
- Emissions from any coal processing and conveying equipment, coal storage system, or coal transfer and loading system processing coal (nonbituminous as well as bituminous coal) may not exceed 20 percent opacity.

3.2.1.1.3 Hazardous Pollutant Emission Standards. The atmospheric emission of several hazardous pollutants is already regulated under Section 112 of the Clean Air Act. Two of these pollutants (beryllium and mercury) are found in coal, but not at levels such that their emission would be expected to violate standards. The establishment of regulations governing arsenic emissions is now under consideration. Other hazardous pollutants under consideration include polycyclic organic matter (POM) and lead, with uncertain decision dates. Except for POM's, emissions of the other hazardous pollutants mentioned above in concentrations likely to be affected by the standards are expected only from sources other than fossil fuel combustion.

3.2.1.1.4 Prevention of Significant Deterioration of Air Quality. A new Part C (Sections 160-169) was incorporated into the Clean Air Act Amendments of 1977 for the prevention of significant deterioration (PSD) of the present ambient air quality. Three land use classes are established, which are interpreted by EPA to have the following characteristics:

- Class I - little or no development
- Class II - scattered development
- Class III - concentrated or large-scale development.

Classification in Class I is mandatory for National parks exceeding 6,000 acres in size and similar state parks and wilderness areas. The verbiage is complex and involved, but the significant fact with respect to coal cleaning processes is that any new source in an area subject to the provisions of this section is to employ the Best Available Control Technology for each pollutant subject to regulation. Consideration of the cost of achieving such emission reduction is not invoked as a factor. Thus, the best available control technology required for prevention of significant deterioration must be better than NSPS. It is obvious that these are site-specific problems, and that a uniform national standard will not be utilized. Each proposed new source will be considered by the affected state on a case-by-case basis, under the state implementation plan. The Act provides for maximum allowable increases in SO<sub>2</sub> and particulates for each class of area, with the provision that the NAAQS shall not be exceeded. Allowable pollutant increases are shown in Table 3-6 along with national primary and secondary ambient air quality standards.

3.2.1.1.5 Visibility Protection for Federal Class I Areas. Section 169 of Part C of the 1977 Amendments specifically addresses the national goal set by the Congress of preventing any future impairment of visibility and remedying any existing impairment from man-made air pollution in mandatory Class I Federal areas. By August 7, 1979, the Administrator shall promulgate regulations to assure reasonable progress toward meeting the national goal. The requirements include existing sources, and may require use of the best available retrofit technology.

3.2.1.1.6 Nonattainment Areas. The new Part D (Sections 171-178) was also incorporated into the Clean Air Act Amendments of 1977, to address alle-

TABLE 3-6. ALLOWABLE POLLUTANT INCREASES ABOVE  
BASELINE CONCENTRATIONS

	Concentration, $\mu\text{g}/\text{m}^3$				
	Class Area			NAAQS	
	I	II	III	Primary	Secondary
<b>Particulate Matter</b>					
Annual geometric mean	5	19	37	75	60
24-hr maximum	10	37	75	260	150
<b>Sulfur Dioxide</b>					
Annual arithmetic mean	2	20	40	80	60
24-hr maximum	5	91	182	365	260
3-hr maximum	25	512	700	-	1,300

violation of air pollution problems in areas where one or more air pollutants exceed any national ambient air standard. Theoretically, no new emission source could be constructed in a nonattainment area. Since this was judged to be an impractical answer, the compromise solution was to require the "lowest achievable emission rate" (LAER). This is an even more restrictive standard than the BACT specified for prevention of significant deterioration. It includes either the most stringent emission limitation for such category of source in any state implementation plan, or the most stringent emission limitation actually achieved in practice, whichever is more stringent. In no event shall it be less restrictive than the NSPS for that category of source. Like prevention of significant deterioration, this is to be implemented by the individual states through the state implementation plans on a case-by-case basis. A key provision is that the states are to continue "reasonable further progress" in achieving annual incremental reductions of the applicable air pollutant, including such reduction in emissions from existing sources in the area as may be obtained through the adoption, at a minimum, of reasonably available control technology (RACT).

The above is part of the so-called "offset" approach, wherein existing emissions are reduced to permit addition of a new source, with the additional constraint that an overall decrease should be shown.

In general, designation as a nonattainment area means that an applicable SIP must be revised to provide for the attainment of the NAAQS as expeditiously as possible. The revised SIP must require permits for the construction and operation of major (>250 T/yr emission of any pollution) new and modified stationary sources, and must contain a prohibition against major new source construction where emissions would contribute to increases in pollutants for which a NAAQS was being exceeded.

The U.S. EPA has published a list of the NAAQS attainment status of all areas within each state.<sup>(21)</sup> This list is revised from time to time.

3.2.1.2 State. Although the U.S. EPA promulgates national ambient air quality standards (NAAQS), states have the privilege of establishing more stringent standards. Thirty-three states and the District of Columbia have ambient air quality standards for one or more pollutants that are more stringent than the NAAQS. Ten of the 19 states with coal preparation plants have



ambient air quality standards (AAQS) that are more stringent than the Federal standards.

Since the concentrations of nitrogen oxides and pollutants other than sulfur oxides and particulates (for which AAQS exist) are only marginally related to the quality of coal prepared or burned, emphasis has been placed on the standards for sulfur dioxide and particulate matter (total suspended particulates). Those states with more stringent AAQS are Alaska, Arizona, California, Connecticut, Colorado, Delaware, Florida, Georgia, Hawaii, Indiana, Kentucky, Louisiana, Maine, Maryland, Minnesota, Mississippi, Missouri, Montana, Nevada, New Hampshire, New Mexico, New York, North Carolina, North Dakota, Ohio, Oregon, South Dakota, Tennessee, Vermont, Washington, West Virginia, Wisconsin, and Wyoming.

States are required to develop state implementation plans which, on approval by the U.S. EPA, specify how the NAAQS or their own state standards, if more stringent, will be achieved within three years of the promulgation of the SIP's. The SIP's cover limitations on existing sources and, where applicable, on new sources. These plans employ different regulatory means for controlling pollutants from fuel-burning equipment. SIP's exist for sulfur dioxide, total suspended particulates, and nitrogen dioxide.

In terms of new source performance standards, all new sources in regulated industry categories must conform to emission limits set by the U.S. EPA, but states are required to develop new source review procedures to ensure that all new sources constructed do not violate NAAQS even if it involves facility resiting or a total denial of a permit to construct a facility.

### 3.2.2 Water Pollution Regulations

3.2.2.1 Federal. There are no national ambient water quality standards analogous to those for air; water pollution is regulated nationally on the basis of emissions, termed effluents in the case of water.

3.2.2.1.1 Effluent Guideline Limitations. The enabling Act providing the authority to establish effluent limitations is the Federal Water Pollution Control Act (FWPCA) Amendments of 1972 (P.L. 92-500). Basic effluent limitations for existing sources have not been promulgated for numerous industries;

others have been challenged by the affected industries and are still in abeyance pending further development. The FWPCA was further amended by the Clean Water Act of 1977 (P.L. 95-217). Effluent guidelines presently are based on the best practicable control technology currently available (BPCTCA), which was to have been achieved by July 1, 1977. By July 1, 1983, effluent limitations were to have required the application of the best available technology economically achievable (BATEA). The Clean Water Act of 1977 extended this date a year to July 1, 1984.

Effluent guidelines are also being promulgated for new sources. These new source performance standards are intended to be the most stringent standards applied.

Federal control of water pollution sources associated with coal preparation and handling is achieved through the issuance of NPDES (National Pollutant Discharge Elimination System) permits to each discharger. These permits limit specific pollutants in the effluents. Effluents from coal cleaning are regulated as a part of the coal mining point source category (40 CFR, Part 434), which defines a "coal preparation plant" as a facility where coal is crushed, screened, sized, cleaned, dried or otherwise prepared and loaded for transit to a consuming facility. The term "associated areas" means the plant yards, immediate access roads, slurry ponds, drainage ponds, coal refuse piles, and coal storage piles and facilities. Regulations have been divided into two groups, one for acidic, and one for alkaline wastes. Final regulations for BATEA effluent limitations have not yet been promulgated.

Regulations for existing plants<sup>(5)</sup> and proposed new source performance standards<sup>(22)</sup> are summarized in Table 3-7.

3.2.2.1.2 Toxic Pollutants. The Clean Water Act of 1977 introduced a new requirement for the control of toxic pollutants, which must be limited by the application of BATEA. Pursuant to this act, the EPA Administrator published a list of 65 toxic pollutants, shown in Table 3-8, for which effluent standards are required. This list of 65 toxic substances and families of substances was identified in the consent decree between EPA and the National Resources Defense Council (NRDC). Regulations previously existed for six of the listed pollutants, but regulations have not yet been

TABLE 3-7. EFFLUENT LIMITATIONS GUIDELINES FOR COAL PREPARATION PLANTS<sup>(5,22)</sup>

Effluent Characteristic	Acidic Wastes <sup>(a,b)</sup>		Alkaline Wastes	
	Daily	30-Day	Daily	30-Day
	Maximum	Average	Maximum	Average
<u>Existing Sources</u>				
TSS, mg/l	70.0	35.0	70.0	35.0
Iron, total, mg/l	7.0	3.5	7.0	3.5
Manganese, total, mg/l	4.0	2.0	-	-
pH, daily range	6.0-9.0		6.0-9.0	
<u>New Source Performance Standards<sup>(c,d)</sup></u>				
TSS, mg/l	70.0	35.0	70.0	35.0
Iron, total, mg/l	3.5	3.0	3.5	3.0
Manganese, total, mg/l	4.0	2.0	-	-
pH, daily range	6.0-9.0		6.0-9.0	

- (a) Excess water effluent from a facility designed to contain or treat the volume of water from the 10-year 24-hour precipitation event not subject to limitations.
- (b) pH may be slightly exceeded to achieve manganese limitation, up to 9.5
- (c) Proposed NSPS.
- (d) No discharge of pollutants from facilities which do not recycle waste water for use in processing.

TABLE 3-8. LIST OF 65 POLLUTANTS BEING CONSIDERED  
FOR EFFLUENT LIMITATIONS<sup>(8)</sup>

1. Acenaphthene	36. Fluoranthene
2. Acrolein	37. Haloethers
3. Acrylonitrile	38. Halomethanes
4. Aldrin/Dieldrin*	39. Heptachlor and metabolites
5. Antimony and compounds	40. Hexachlorobutadiene
6. Arsenic and compounds	41. Hexachlorocyclohexane
7. Asbestos	42. Hexachlorocyclopentadiene
8. Benzene	43. Isophorone
9. Benzidine*	44. Lead and compounds
10. Beryllium and compounds	45. Mercury and compounds
11. Cadmium and compounds	46. Naphthalene
12. Carbon tetrachloride	47. Nickel and compounds
13. Chlordane	48. Nitrobenzene
14. Chlorinated benzenes	49. Nitrophenols
15. Chlorinated ethanes	50. Nitrosamines
16. Chloroalkyl ethers	51. Pentachlorophenol
17. Chlorinated naphthalene	52. Phenol
18. Chlorinated phenols	53. Phthalate esters
19. Chloroform	54. Polychlorinated biphenyls (PCB's)*
20. 2-chlorophenol	55. Polynuclear aromatic hydrocarbons
21. Chromium and compounds	56. Selenium and compounds
22. Copper and compounds	57. Silver and compounds
23. Cyanides	58. 2,3,7,8-Tetrachlorodibenzo-p-dioxin
24. DDT and metabolites*	59. Tetrachloroethylene
25. Dichlorobenzenes	60. Thallium and compounds
26. Dichlorobenzidine	61. Toluene
27. Dichloroethylenes	62. Toxaphene*
28. 2,4-dichlorophenol	63. Trichloroethylene
29. Dichloropropane and dichloropropene	64. Vinyl chloride
30. 2,4-dimethylphenol	65. Zinc and compounds
31. Dinitrotoluene	
32. Diphenylhydrazine	
33. Endosulfan and metabolites	
34. Endrin* and metabolites	
35. Ethylbenzene	

\* Pollutants for which regulations have been promulgated.

promulgated for any of the other listed pollutants. EPA has further identified specific compounds, within the chemical classes in the published list, to be considered for effluent standards. The thirteen elements in the published list, and their compounds, should receive emphasis in the environmental assessment of coal cleaning processes because of observed existence in coal. However, none of the classes of organic chemicals in the list appears to have significance as a pollutant from coal cleaning processes because they have not been observed to exist in coal and have not been used as agents in coal cleaning operations.

3.2.2.1.3 Water Quality Criteria. While ambient air quality standards are set at the Federal level, water quality standards are primarily a state responsibility. The only existing Federal water quality standards are those for drinking water, applicable to public (community) water supplies. Maximum contaminant levels in public water supplies have been set for the following contaminants that are associated with coal and coal activities: arsenic, barium, cadmium, chromium, fluoride, lead, mercury, nitrate, selenium, and silver.

Federal water quality criteria (guidelines) have recently been revised and expanded, and published by the U.S. EPA.<sup>(6)</sup> While these criteria do not have direct regulatory application, the states are expected to adopt these in implementing state water quality regulations. The criteria are two-fold. In one instance, the goal is water quality that will provide for the protection and propagation of fish and other aquatic life and for recreation in and on the water. Criteria are also presented for domestic water supply use. These suggested limits were used in this study in developing estimated permissible concentrations (EPC's) for the pollutants listed.

3.2.2.2 State. The situation on control of water pollution by the states is analogous to that for air pollution. Emission standards (effluent guidelines) are established on a national level by EPA, but their implementation is regarded as a state responsibility. The Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) provides for the reduction of duplicate laws by delegating permit issuance authority to the states. Delegation of authority takes place when a state demonstrates that it has legal

authority and resources to operate the program as envisioned by that Federal law. The States of Colorado, Indiana, Kansas, Maryland, Missouri, Montana, North Dakota, Ohio, Virginia, Washington, and Wyoming are delegated NPDES-issuing states. The effluent limitations vary among the delegated and non-delegated states.

Water pollution control enforcement is based on effluent standards rather than stream quality, and plant discharges must be within certain limits prescribed for each industry. The objective of such control systems is to achieve or maintain ambient water quality standards which are primarily a state responsibility. If these are not achieved by compliance with effluent standards, more stringent limits may be applied.

### 3.2.3 Solid Waste Regulations

3.2.3.1 Federal. Prior to October 21, 1976, protection of the environment from pollution arising from the land disposal of solid wastes was provided by the Solid Waste Disposal Act of 1965 (P.L. 89-272), as amended by the Resource Recovery Act of 1970 (P.L. 91-512). Federal guidelines for the Land Disposal of Solid Wastes are given in Title 40 CFR, Part 241. (23)

Pursuant to Section 211 of the Solid Waste Disposal Act as Amended in 1970, the guidelines are mandatory for Federal agencies and are recommended to state, interstate, regional, and local governmental agencies for use in their solid waste disposal activities. However, these are only guidelines, and do not establish new standards, but set forth requirements and recommended procedures to ensure that the design, construction, and operation provide for environmentally acceptable land disposal site operations. The thrust of Part 241 is towards sanitary and municipal wastes. Mining wastes are essentially ignored.

The management of solid and hazardous wastes entered a new era on October 21, 1976, with passage of the comprehensive Resource Conservation and Recovery Act (RCRA) of 1976 (P.L. 94-580). Although this Act is not yet implemented, it is already clear that the management of solid and hazardous wastes will be revolutionized by the specific regulations that are currently being drafted by the U.S. EPA.

The introductory section of the Act describes the Federal role as one of providing financial and technical assistance and leadership in the development, demonstration, and application of new and improved methods of waste management. In practice, it appears that guidelines and regulations will be developed by the U.S. EPA, for adoption and promulgation by the states, possibly in a fashion similar to the SIP's used for air pollution control. The individual states would enforce their adopted regulations.

Some of the general provisions of the Act are:

- The U.S. EPA was to issue guidelines by October 21, 1977, for defining sanitary landfills as the only acceptable land disposal alternative which can be implemented; open dumps are to be prohibited.
- By October 21, 1977, the U.S. EPA was to develop and publish suggested guidelines for solid waste management.
- By April 21, 1978, the U.S. EPA was to promulgate criteria for identifying hazardous waste; standards for generators and transporters; and standards for treatment, storage, and disposal of hazardous wastes.
- Permit programs are to be managed by the states under minimum guidelines provided by the U.S. EPA.
- Each regulation promulgated shall be reviewed and, where necessary, revised at least every three years.

The development of specific regulations is appreciably behind schedule, and discussion of possible requirements is, accordingly, unavoidably speculative. However, it is evident that very great attention will be given to those wastes classified as hazardous. The criteria for their identification and classification have not yet been proposed; the boundaries finally selected will have a major impact upon waste management. It is presently uncertain whether coal refuse (and combustion ash) will be classified as non-hazardous wastes, which would avoid the most restrictive provisions of the Act. In the absence of developed regulations, it is not possible at this time to delineate either the details of its application or its impact upon coal cleaning.

The Geological Survey of the U.S. Department of the Interior has established regulations for the disposal of wastes from coal preparation plants located on the surface of land associated with mining.<sup>(24)</sup> Preparation is defined as any crushing, sizing, cleaning, drying, mixing, or other processing

of coal to prepare it for market. The operator is required to:

"dispose of all waste resulting from the mining and preparation of coal in a manner designed to minimize, control, or prevent air and water pollution and the hazards of ignition and combustion."

Additionally, more specific requirements are given for waste pile construction, covering, and revegetation, and for settling ponds.

3.2.3.2 State. A few states have solid waste disposal regulations directly applicable to coal preparation or consumption. The various states have general regulations covering solid waste management, solid waste disposal, and solid waste disposal areas (landfills, sanitary landfills, etc.). Solid wastes are not to be disposed of in a place or in a manner that will endanger human health and plant or animal life or contribute to air pollution. Disposal areas are to be located to ensure the least possibility of contaminating surface or ground waters. The provisions of the Resource Conservation and Recovery Act of 1976 will allow definitive guidelines to be established by each state for the storage and disposal of solid wastes, including those generated from coal preparation and consumption.



### 3.3 References

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#### 4.0 ESTIMATION OF ENVIRONMENTAL CONCENTRATIONS

Eventually, emissions and environmental concentrations at coal cleaning plants will be measured rather than estimated. For the present, however, it is necessary to estimate these concentrations using appropriate models. The approaches to estimating emissions are described in Section 4.1, followed by discussions of physical transport and dispersion (Section 4.2) and ecological transport and distribution (Section 4.3).

##### 4.1 Modeling of Pollutant Emissions

By virtue of its origin, coal has been found to contain nearly every naturally-occurring element. The concentrations of these elements in coal vary widely. Many of these elements, e.g., arsenic, beryllium, cadmium, lead, and mercury are recognized as toxic substances.

The various lists of potential pollutants described earlier (Section 3.1.1) identify those pollutants that may be of concern in coal cleaning, provided that they are present and emitted above some yet undefined rate of release and/or concentration. The ranges of pollutant concentrations characteristic of coals (Section 3.1.2) provide some information on their presence but none on their possible emissions. The first item needed to estimate emissions is information on the process steps embodied in the cleaning flowsheet (these are a "given"). Many alternatives and combinations of alternatives are possible in crushing, sizing, and washing coal, and in separating coal from refuse. The actual combination of process elements will influence the degree of pollutant emissions but not the kind. Thus, for purposes of developing assessment criteria and methodology, reasonable approximations of a generic process flowsheet will suffice and are used in this report.

#### 4.1.1 Fractionation Factors

The second item needed for estimating emissions is information on "fractionation factors", i.e., the distribution of substances in raw coal to another fraction or phase as the coal passes each process step. Examples are coal:refuse, in cleaning; and coal:ash and coal:atmosphere in combustion.

One way of classifying noncombustible components in coal is to characterize the mineral matter as either "inherent" or "extrinsic, extraneous, or adventitious". Inherent mineral matter is usually defined as that portion of mineral matter originally combined with the coal.<sup>(1)</sup> It cannot be detected petrographically or separated by physical methods. These constituents would be considered as having a high "organic affinity". Extrinsic or adventitious mineral matter is readily detected petrographically and more or less readily separated from coal. It may have originated during coal formation (syngenetic) or after the coal had formed (epigenetic). Extrinsic constituents would have a low "organic affinity". The degree of organic affinity is useful in predicting the distribution of elements between coal and refuse in coal cleaning. The theoretical aspects of this have been examined by Zubovic and coworkers at the U.S. Geological Survey.<sup>(2)</sup> Zubovic postulated that trace metals in coal are present in the organic phase as chelated metal organic complexes. Metal ions with a high ratio of ionic charge to ion radius would be the preferred species undergoing complex formation and would have higher organic affinity. Experimental data supported the existence of such complex formations.

There may be some correlation between the fractionation factor and the ionic potential of the element. Figure 4-1 plots fractionation factors of trace elements, estimated from float-sink experiments, against ionic potential (the ratio of ionic charge to ion radius for each element). Although the data are somewhat scattered, there is a correlation between the two parameters; i.e., the fractionation factors tend to increase as the ionic potential increases. The fractionation factors can be approximated as a function of the ionic strength, and they generally fall in the range between the two straight lines drawn in Figure 4-1. In Battelle's

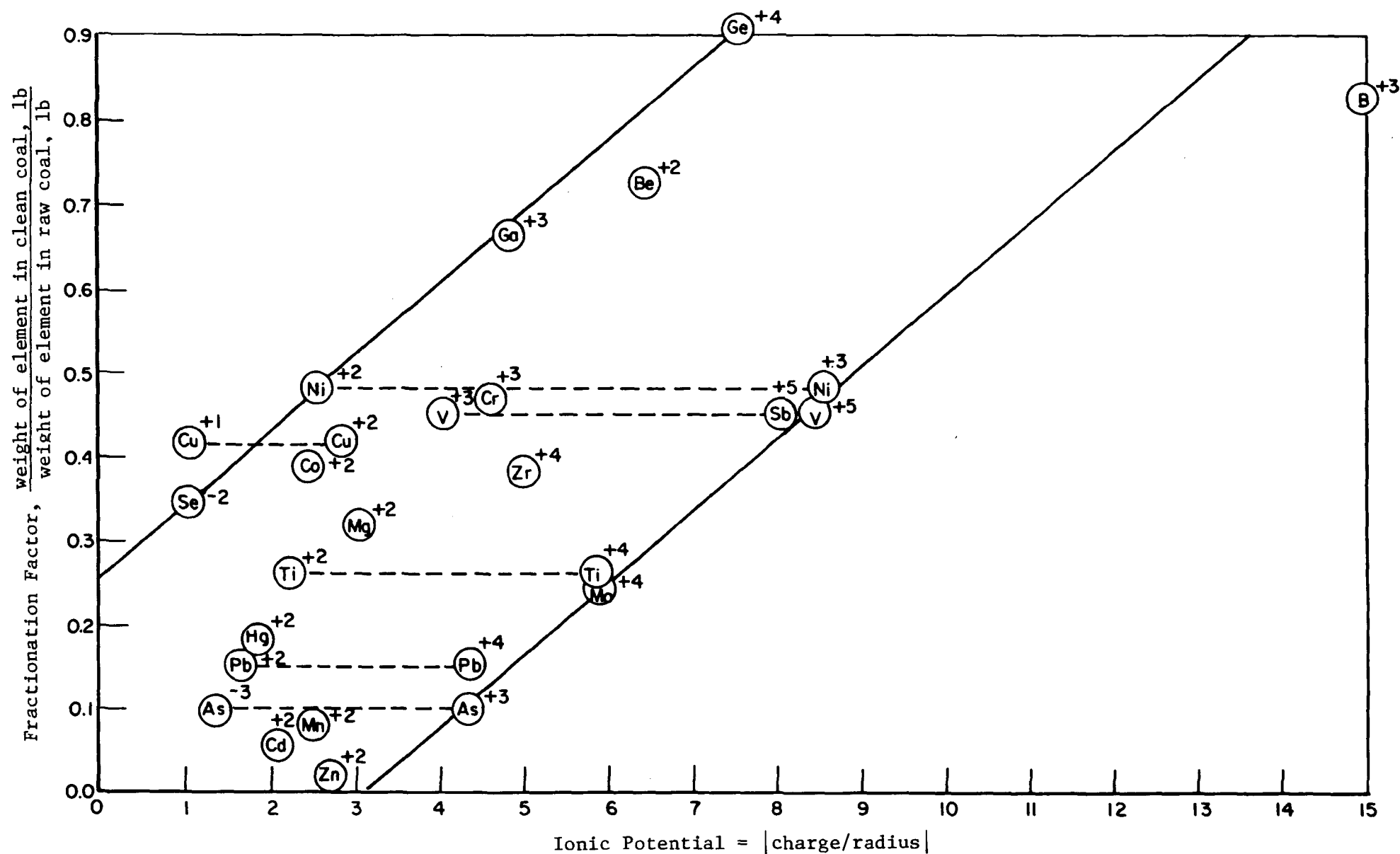


FIGURE 4-1. FRACTIONATION FACTOR VERSUS IONIC POTENTIAL

preliminary draft report on development of environmental assessment criteria <sup>(3)</sup>, fractionation factor ranges were estimated for a number of elements using this approach. This approach may be useful for estimating the upper and lower limits of the fractionation factors for trace elements for which no experimental data are available. However, it suffers from the fundamental fact that coals are not alike, and an element may not be consistently associated with either the organic or the inorganic fraction, from one coal to another.

More useful than fractionation factors are empirical data based on laboratory experiments. Float-sink, or washability data, have been compiled for many coals. Gluskoter, et al., <sup>(4)</sup> have examined this aspect of coals intensively, concentrating on Illinois Basin coals, but also including numerous other Eastern coals.

In one series of extensive washability tests of four Illinois Basin coals, three Appalachian coals, and one Arizona coal, they found, not surprisingly, that the Illinois coals were much more similar to each other with regard to organic affinities than they were to coals from other areas. It was possible to make several generalizations for these coals:

- Ge, Be, B, and Sb tended to have the highest organic affinities
- Zn, Cd, Mn, As, Mo, and Fe tended to have the lowest organic affinities
- A number of metals including Co, Ni, Cu, Cr, and Se, were intermediate in value, suggesting a partial contribution from sulfide minerals in the coal, along with the presence of organometallic compounds that contain these elements, or the presence of chelated species and/or adsorbed cations.

The grouping of these elements is generally consistent with the ordering based on ionic potential (Figure 4-1). Gluskoter, et al., observed that as Appalachian and Arizona coals were included, the number of generalizations possible decreased.

They classified the elements into four groups:

Organic	Intermediate-inorganic
Intermediate-organic	Inorganic.

The "organic affinity" indices separating the groups varied from coal to coal; similarly, some elements occasionally shifted from one group to the next. It is clear that no hard and fast grouping is possible for all elements in all coals, and the rankings are perhaps better expressed as tendencies. For the purposes of investigating environmental assessment criteria, "average" behaviors of the elements generally have been utilized.

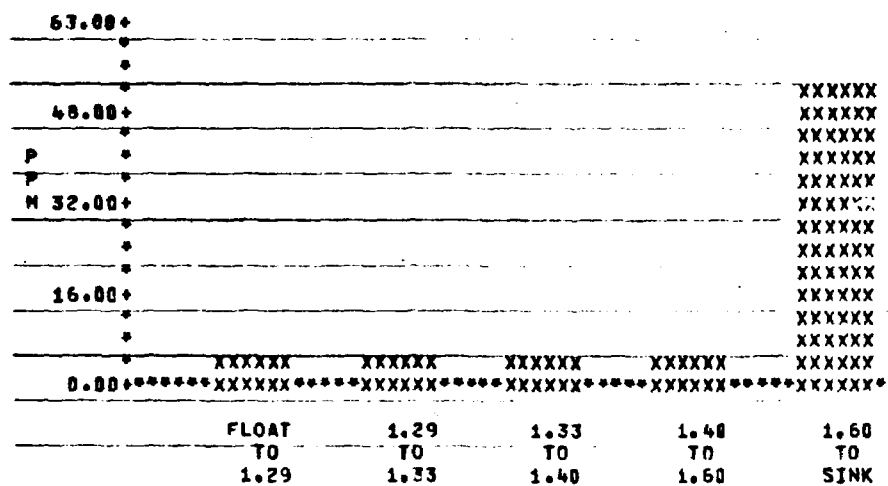
If it is desirable to base the calculations on a specific coal, for which washability data are available, fractionation factors calculated for that coal can be used. A simple computer program has been developed and tested which permits estimation of fractionation factors for elements as a function of specific gravity separation points and/or yield. Illustrative are the computer plots for arsenic in Herrin No. 6 Illinois coal (Figure 4-2), based on the data of Gluskoter, et al.<sup>(4)</sup>

Calculating the fractionation factors for a particular constituent of a particular coal requires data on the ppm of that constituent by specific gravity fraction and the total weight of material in each specific gravity fraction. The first step in the calculation is to compute cumulative ppm of the constituent from lightest specific gravity fraction to heaviest and cumulative weight in these fractions. Dividing the cumulative weight values by the total weight gives yield. Cumulative ppm versus yield is shown in Figure 4-2 (b).

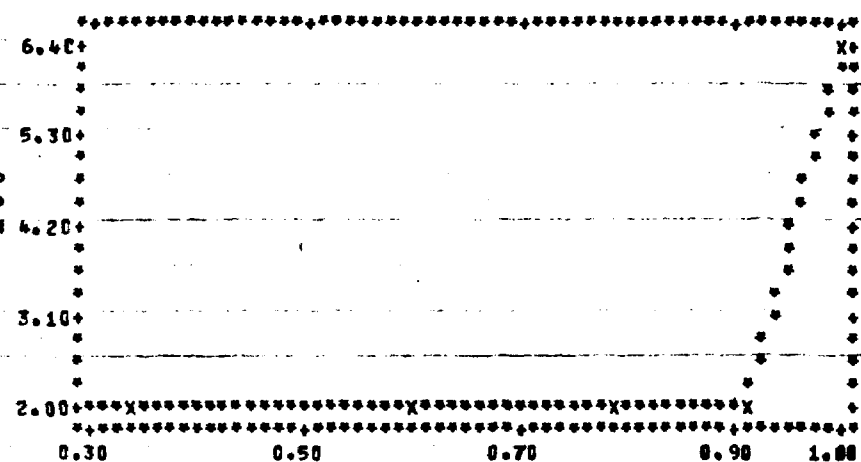
Now the fractionation factor is simply that portion of the total amount of the constituent in each specific gravity fraction, shown plotted against yield in Figure 4-2 (c). Finally, the fractionation factors are plotted against the midpoints of the specific gravity fractions in Figure 4-2 (d).

"Fractionation factors" are also available from Klein, et al.,<sup>(5)</sup> and others, for the partitioning of elements upon combustion in a boiler. These can be used to estimate losses to the atmosphere from the thermal drying of cleaned coal. For partitioning of elements between coal and the atmosphere during transport, handling, and storage, "fractionation factors" would correspond to emission factors, such as those estimated by EPA<sup>(6)</sup> and others.<sup>(7)</sup> Analogous "emission factors"

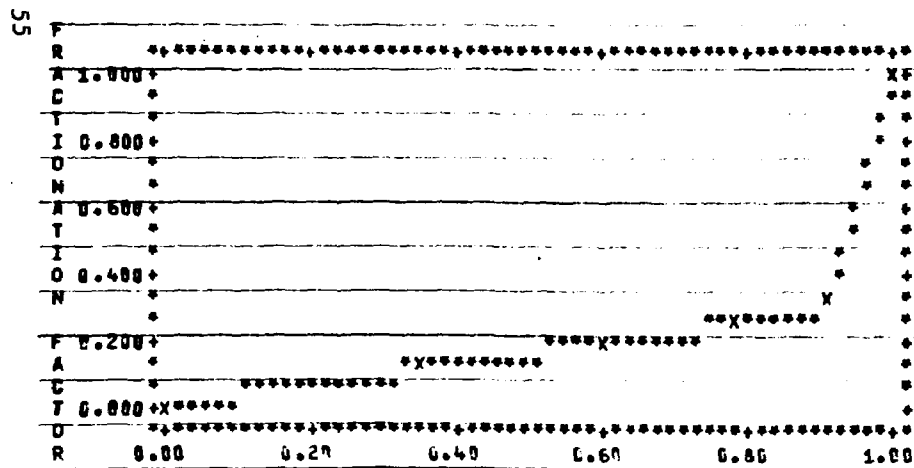




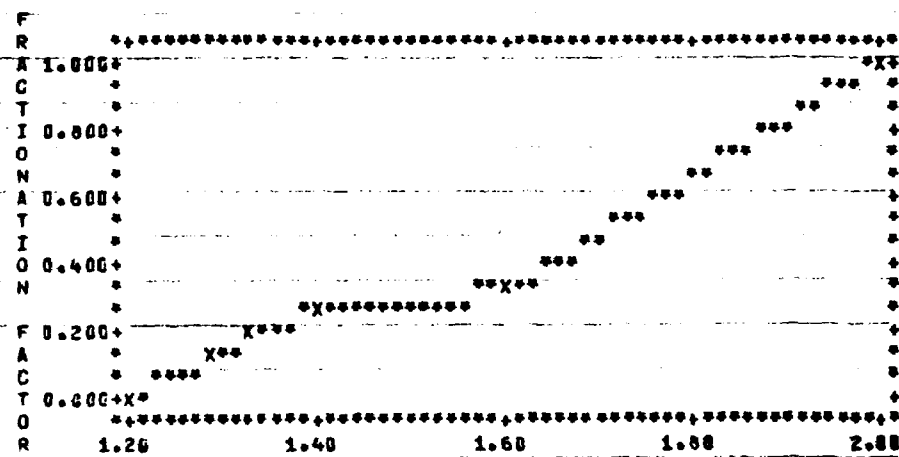
(a) Specific Gravity Fraction



(b) Yield



(c) Yield



(d) Specific Gravity of Separation

Note: X indicates an observed point, while \* indicates an interpolated point.

FIGURE 4-2. CALCULATION OF FRACTIONATION FACTORS, ARSENIC, HERRIN (NO. 6), ILLINOIS (FLOAT-SINK SET 1)

have yet to be developed for losses of pollutants leached out from coal storage piles, ash ponds, etc.

#### 4.1.2. Estimation of Emission Concentrations

Values of emission concentrations are required as input to dispersion models to permit the calculation of ground level concentrations (GLC) for air pollutants and surface water concentrations (SWC) for water pollutants. A simplified preliminary material balance model has been developed covering the direct process steps from raw coal to combusted ash, illustrated by Figure 4-3. The incidental losses to air and water arising from transportation, handling, and storage are not included in this preliminary model, but can readily be included when data become available. The model, which is normalized to a combustion output of  $10^6$  Btu, can provide estimates of absolute emissions and average concentrations of any number of trace constituents in (1) recirculated water, (2) thermal dryer atmospheric discharge, (3) stack discharge from combustion, and (4) ash flow based on composite flows, given an analysis for the starting raw coal.

The model has been derived, programmed, and run with example cases, using a composite fuel analysis of 68 percent coal from the Helvetia mine and 32 percent coal from the mine simulating feed to the Homer City coal cleaning plant.\* The results of a recent run of this model, using an assumed 80 percent coal recovery, and fractionation factors based on the float-sink data of Gluskoter, et al.,<sup>(4)</sup> for 3/8-in. x 28 mesh Pittsburgh No. 8 coal, are shown in Appendix A.

Only a few elements are shown in the illustrative example in Appendix A. These can be expanded to include all elements for which fractionation factors are available or can be estimated. In this example,

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\* This MCCC (Multistream coal cleaning system) facility, to be in operation in 1978, is located near the Homer City Generating Station Power Complex, Homer City, Pennsylvania. The coal cleaning facility is owned by Pennsylvania Electric Company (a subsidiary of General Public Utilities Corporation) and New York State Electric and Gas Corporation.

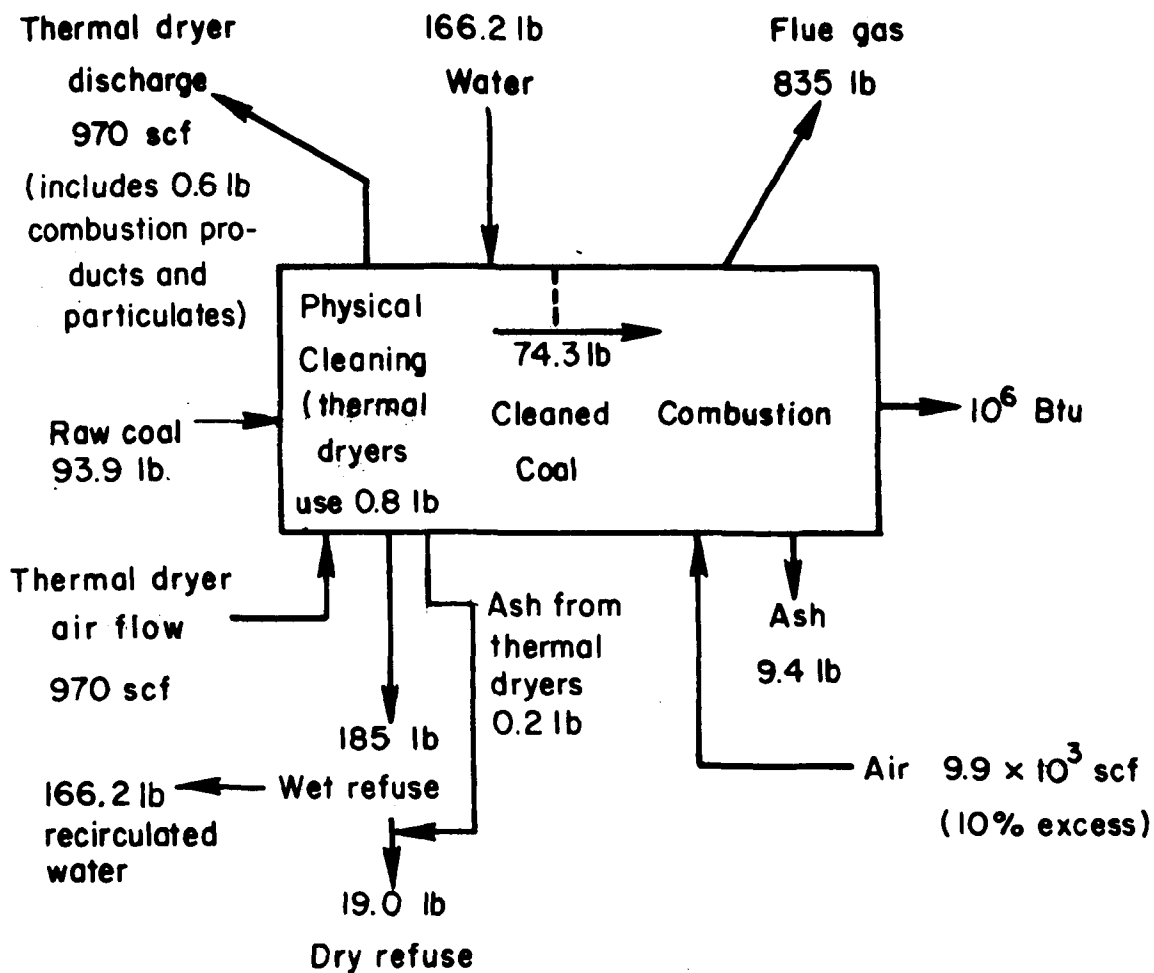


FIGURE 4-3. GENERALIZED FLOW QUANTITIES IN COAL CLEANING PROCESS

application of some control technology was assumed. The use of a Venturi scrubber was assumed for the thermal dryer exhaust (efficiencies based on Abel, et al.<sup>(8)</sup>) and use of an electrostatic precipitator on the boiler ultimately burning the coal was assumed. Other control technology alternatives can be substituted.

#### 4.2 Modeling of Physical Transport and Distribution

Pollutants emitted in the course of coal cleaning, handling, transportation, storage, and combustion can both accumulate and disperse, in both a physical and biological sense, depending upon the characteristics of the pollutant and the compartment. Biological transport and fate are discussed in Section 4.3. In this section, modeling of the preceding physical transport and dispersion are discussed. The general need for modeling is to make estimates of the concentrations of trace pollutants in environmental media as a result of operation of a coal cleaning plant. No regulations or design criteria are available yet for most of these, although regulations will be proposed and promulgated by EPA within the next year or two for a number of toxic pollutants (see Section 4.2.2), which may affect coal cleaning plants.

In succeeding paragraphs, modeling approaches are discussed relative to surface water, groundwater, air, and porous media. Generally, the air pollution model should account for deposition, both wet and dry, providing one input to surface water and soils. Surface water run-off will pick up material in the upper soil layer. The coal pile will be leached by precipitation, which will also generally be carried into surface water. Leaching and leakage through sedimentation pond bottoms will generally contribute to groundwater pollution, although the movement of some pollutants through the subsoil and into the groundwater requires years because of adsorption of materials on soils. The refuse area, usually some kind of a fill, will be leached by the downflow of water from precipitation and surface flow, contributing to both stream pollution and groundwater pollution. The rationale that should be incorporated in the modeling approach is to build a capability of evaluating individual coal cleaning complexes, either existing or

under design. This approach is recommended because the many different characteristics, e.g., meteorology, topography, stream geometry, soil, and groundwater characteristics required to characterize a given complex, vary widely from one plant to another, making generalizations risky at this time.

On the other hand, the objective of the present investigation is to develop criteria and associated methodologies for their application rather than to estimate site-specific environmental impacts for a given complex. The solution would seem to be to include the necessary provisions in the models for the multiplicity of detailed parameters that will ultimately be required, but to use nominal values, or ranges, or possibly even "worst-case" estimates, for a hypothetical site in the developmental phase.

Validation is an important aspect of model development, and should be planned for, utilizing one of the coal cleaning sites chosen for field data acquisition. Field data will permit validation and calibration of the models and suggest their application for future sites. However, it is not possible within the time frame of the present program to wait until field data are available to initiate model development. For that matter, it is not desirable to wait because modeling will define data that need to be gathered and will give preliminary evaluations, using data that are available in the literature from other areas.

A review of models for air, water, and groundwater quality assessment, which are applicable to coal cleaning, has been compiled by Ambrose, et al.<sup>(9)</sup>

#### 4.2.1 Air Dispersion of Pollutants

The concentration of key pollutants in the thermal dryer atmospheric discharge and in the flue gases from combustion of the cleaned coal will provide input for calculations of atmospheric dispersion. The basic purpose of the dispersion calculation is to provide an estimate of the dilution factor which, when divided into the stack emission concentrations, will yield ground level concentrations.

Two basic models are required, depending on whether the pollutant is associated with large ( $> 100 \mu\text{m}$ ) or small ( $< 100 \mu\text{m}$ ) particles. Large particles tend to deposit on surfaces near the stack so that their concentration in the air diminishes as distance from the stack increases. The concentration of smaller particles is reduced only by dispersion.

Simplified dispersion models, typified by that presented by Turner,<sup>(10)</sup> are available that consider stack height and diameter, stack gas temperature and exit velocity, and ambient air temperature and wind speed. Calculations are performed for different weather categories. Multiple sources can be considered to include the effects of more than one stack if distance between stacks is large enough to merit this refinement.

The large particle deposition model requires only the deposition factor, wind speed, and effective stack height. Deposition factors are available in the literature for various wind speeds of interest.

A fugitive dust emission model, based on the EPA Multiple Point Source Model (PTMTP), has been used by Battelle to help in selecting environmental sampling sites and to project mass atmospheric concentrations. It is a Gaussian plume, multiple-source model, with a generation function for fugitive emissions dependent on wind speed squared. Deposition is accounted for (but not plume depletion), and the model has been calibrated by Battelle based on field data. The operation of this model has been described.<sup>(11)</sup> The model may require modification to account for wet deposition which has been shown to account for far more than half of the deposition of Cd, Hg, Pb, and other trace elements in eastern Tennessee (from power plant plumes)<sup>(12)</sup>. Experimental deposition velocities are also available<sup>(12)</sup>.

#### 4.2.2 Water Dispersion of Pollutants

Two types of effects may need consideration when modeling pollutant discharges to water: (1) dispersion and sedimentation of particulate solids, and (2) dispersion and dilution of soluble pollutants.

For estimating surface water concentrations, data on the concentration of pollutants and the flow of waste discharges are required. Emission

sources to be considered include the waste water discharge from coal cleaning, and runoff and percolation from coal and refuse storage piles, as well as from ash ponds at coal cleaning plants and from coal storage piles at user plants.

Sedimentation in settling basins can be modeled by the use of deposition coefficients. Since sedimentation removes only a portion of the pollutant from a water column, a residual concentration remains which is then further diluted by dispersion and additional sedimentation in streams, etc. Simplified dispersion models using point sources of pollutants can be used. These models provide a correlation of dispersion coefficient with flow velocity and stream configuration so that reasonable approximations for surface water concentrations associated either with a specific facility or with a generalized case can be calculated for average flows, low flows, and high flows. Sedimentation is incorporated by using deposition factors that relate sedimentation rate to pollutant concentration in the water body. Output consists of sedimentation rate and concentration in water as a function of position (normally distance downstream) for each case. Pseudo-steady state models are believed to be adequate. With these models, when conditions such as release rates or flow of the stream change, concentrations make a step change from one steady state to another. Sediment accumulates on the stream bottom linearly with time until such a change in conditions occurs.

Fully mixed (with stream cross section and depth) models are more appropriate for small narrow streams, which are likely to be around a coal cleaning plant. In such a case, the stream concentration,  $C_A$ , for pollutant A is given by

$$C_A = \left( \frac{R_A}{Q} \right) \exp (-k_A t) \quad (1)$$

where  $R_A$  is the release rate of pollutant A (gm/day),  $Q$  is the stream discharge rate ( $m^3$ /day),  $k_A$  is the sedimentation coefficient for pollutant A ( $day^{-1}$ ), and  $t$  is the travel time (days) to the downstream position of interest.

$$t \text{ is defined by } \frac{\int_0^x w dx}{Q}$$

where  $x$  is the distance downstream,  $w$  is the stream width, and  $d$  is the stream depth (note that  $w$  and  $d$  can be variable). For a stream with a uniform cross section,  $t$  is simply  $x/V$  where  $V$  is stream velocity (m/day).  $k_A$  is equal to  $k_{bA}/d$  where  $k_{bA}$  is a bottom deposition coefficient (m/day) and  $d$  is the depth.

The flux of pollutant A to the bottom at any given location is given by  $k_{bA} C_A$ .

In the case of a shoreline release to a large stream, it may be advantageous to use a two-dimensional model, using dispersion in the cross stream direction as the mixing mode. In such a case,  $C_A(t,y)$  is given by

$$C_A(t,y) = \frac{R_A w}{Q \sqrt{\pi D t}} \exp \left[ -k_A t - \frac{y^2}{(4Dt)} \right] \quad (2)$$

$C_A(t,y)$  is dependent on both downstream travel time (or position) and cross-stream position,  $y$ .  $D$  is the dispersion coefficient, which is characterized by stream geometry and flow rate. Sedimentation at a given location is calculated by  $k_{bA} C_A(t,y)$ .

These solutions to the transport equation have been known for years, and they are reasonably applicable for continuously flowing freshwater streams.

The need for a sedimentation model is not certain. The U.S. EPA has promulgated effluent guidelines for existing coal preparation plants and associated areas<sup>(13)</sup> and also has proposed new source performance standards<sup>(14)</sup>, both of which establish upper limits of total suspended solids (TSS) of 70 mg/l (maximum for any one day) and 35 mg/l (average of daily values for 30 consecutive days). For new sources, these values apply to facilities that recycle waste water for use in processing (nearly all new facilities should fall into this category). A "no-discharge-of-process-waste-water" limitation is proposed for new facilities that do not recycle waste water.

The definition of "coal preparation plant associated areas" is broad, including plant yards, immediate access roads, slurry ponds, drainage ponds, coal refuse piles, and coal storage piles and facilities<sup>(13)</sup>. Thus, in order to be in compliance, effluent from all areas of a coal preparation plant, including coal and refuse piles, will have to be controlled so that



the total aqueous TSS discharge does not exceed a 30-day average of 35 mg/l. At this concentration, sedimentation probably can be neglected.

#### 4.2.3 Dispersion Through Porous Media

Although emission of pollutants to the atmosphere and to surface waters is regulated by the U.S. EPA, heretofore the invisible and difficult-to-measure escape of aqueous pollutants downward through the soil has essentially avoided regulation. This situation is beginning to change, and this pollutant transport path should be considered in regard to environmental criteria for coal cleaning plants. As indicated in the introduction to this section, this pollutant release pathway can come into play beneath storage piles of raw and cleaned coal or refuse, as well as under refuse ponds.

Simplified approaches to modeling adsorption and leaching of pollutants in porous media are available. Simplified one-dimensional models are described by Raines<sup>(15)</sup> along with comparisons with sophisticated results such as computerized finite difference models with Langmuir adsorption-desorption. In many cases, the simplified models are quite adequate. It is recommended that initial emphasis be directed toward correlation of data and estimation with these models.

One simplified solution for adsorption is given by

$$C_A(\tau, z) = \frac{1}{2} C_{A(IN)} \left[ 1 - \operatorname{erf} \left( \frac{z - \tau^*}{2 \sqrt{N_D \tau^*}} \right) \right] \quad (3)$$

where  $C_A(\tau, z)$  is the concentration of pollutant A in the liquid at any relative position  $z$  in the porous medium and at any normalized time,  $\tau$ .  $\tau$  is given by  $t/\theta$ , where  $t$  is real time and  $\theta$  is the residence time for the bulk fluid.  $C_{A(IN)}$  is the concentration in the liquid at the point where it enters the porous medium.  $\tau^*$  is the ratio  $\tau/(1+K_E)$  where  $K_E$  is a linear equilibrium constant for the adsorption/desorption process.  $N_D$  is the dispersion parameter,  $D/(VL)$ , where  $D$  is the dispersion coefficient,  $V$  is the average liquid velocity, and  $L$  is the characteristic length of the porous medium. The notation  $\operatorname{erf}$  denotes the error function which is tabulated in standard references. This solution assumes local equilibrium,

i.e., the concentration of adsorbed pollutant A is always in equilibrium with the liquid concentration immediately adjacent to it.

The concentration of pollutant A leaving the porous body after adsorption is given by

$$C_{AEa} = C_A(\tau, 1) = \frac{1}{2} C_{A(IN)} \left[ 1 - \operatorname{erf} \left( \frac{1 - \tau^*}{2 \sqrt{N_D \tau^*}} \right) \right] \quad (4)$$

The analogous solution for desorption is

$$C_A(\tau, 1) = \frac{1}{2} C_{AO} \left[ 1 + \operatorname{erf} \left( \frac{z - \tau^*}{2 \sqrt{N_D \tau^*}} \right) \right] \quad (5)$$

where  $C_{AO}$  is the concentration in the fluid phase during the adsorption step.

The concentration of pollutant A leaving the porous body after desorption is given by

$$C_{AEd} = C_A(\tau, 1) = \frac{1}{2} C_{AO} \left[ 1 + \operatorname{erf} \left( \frac{1 - \tau^*}{2 \sqrt{N_D \tau^*}} \right) \right] \quad (6)$$

Plotting of either  $C_{AEa}/C_{A(IN)}$  or  $C_{AEd}/C_{AO}$  on a probability scale versus  $(\tau^* - 1)/\sqrt{\tau^*}$  yields a straight line with the 0.5 value occurring at  $\tau^* = 1$ . This model says that a given exit concentration that would be achieved at a value  $\tau$  with no adsorption or desorption will not occur until  $(1 + K_E)\tau$  with adsorption or desorption present.

The simplified concept for leaching of coal piles or refuse areas would employ Equation (6) where  $C_{AO}$  is equal to the concentration in water in equilibrium with the trace element concentration in the coal or refuse.

#### 4.2.4 Groundwater Dispersion of Pollutants

Groundwater modeling for accurate estimation of flows and resulting trace contamination is sophisticated and complicated. A sophisticated approach is not deemed within the scope of this program at the present time. The recommended approach consists of specifying a groundwater flow rate and then using Equation (3) to estimate the concentration of pollutant A in the groundwater at various locations and times of interest. <sup>(15)</sup>

Experimental data for various trace elements and various soils are available <sup>(16)</sup> from which approximate  $K_E$  values can be determined. The data given in Reference (16) are plots from experimental adsorption in soil

columns; a graph of  $C_{AEa}/C_{A(IN)}$  for the different element-soil combinations versus the number of pore volumes of liquid passed through the column were given. The number of pore volumes is identical to the parameter,  $\tau$ , in the simplified model. Thus,  $K_E$  is estimated by subtracting one from the value of  $\tau$  at which an experimental value of 0.5 for  $C_{AEa}/C_{A(IN)}$  is obtained. Estimates for As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn in 10 soils are available. The soils include variations of sands, loams, and clays. Results range from  $K_E = 0$  (no adsorption) to no detectable trace element in the effluent for the duration of the experiment, which, in these particular experiments, corresponds to a  $K_E$  greater than about 30.

Hg was the most mobile of the trace elements tested,<sup>(16)</sup> showing at least some pass-through for all soils tested. Cd was highly mobile ( $K_E \approx 0$ ) in two soils: Wagram, a loamy sand from North Carolina, and Ava, a silty clay loam from Illinois. Numerical values for results are not given in the Korte paper,<sup>(16)</sup> and it probably will be desirable to try to obtain the numerical data from the authors.

#### 4.3 Ecological Transport and Distribution

In order to assess the ecological effects of the release of pollutants from coal cleaning processes, an elucidation of their ecological transport and fate is necessary. The pollutant's chemical form, concentration, and mode of entry into the ecological system (i.e., atmosphere, food source, or water) depends on the coal type, environmental conditions, and type of coal cleaning technology employed at a facility. The ultimate concern when dealing with ecological fate is the rate at which the toxicant or pollutant moves within the ecosystem and whether or not the pollutant biomagnifies within its various components.

Requirements for implementing a quantitative study focused on determining the ecological transfer of a toxicant are extremely rigorous. Recent investigations have shown that the variability in a pollutant's chemistry, specific target ecosystem, source release rate, abiotic dispersion factors and the environmental factors (i.e. soil type, etc.) affect the ability to accurately quantify ecological transport of pollutants. This quantification requires knowledge of general soil or sediment parameters, dominant

vegetative species composition, and other important parameters to accurately calculate potential rates of movement and specific target organisms' body burdens. Such information cannot be extracted from the literature. Most researchers have avoided or ignored these confounding parameters altogether, thus adding to the general misunderstandings of pollutant transport rate and ultimate fate reported in the literature. It is not that reported values are incorrect or inadequate, but that dominant influencing parameters are not being adequately characterized. As a result, these investigators cannot adequately estimate movement of the pollutant in the environment with respect to time.

Investigation of the entire list of Priority 1 pollutants (see Table 3-1) was beyond the scope of this subtask, which focused on the abbreviated "short list" extracted from that group. Since sulfur and nitrogen are part of the biological cycle, they were eliminated, and the following eight elements were investigated.

- Arsenic
- Beryllium
- Cadmium
- Iron
- Lead
- Manganese
- Mercury
- Selenium.

The specific objectives of this aspect of the study were to:

- Identify the typical components of the generic ecosystem that are most likely to receive process wastes from a coal cleaning facility
- Determine the dominant pathways that are likely to control pollutant transport through a generic food web
- Determine which of the designated pollutants are most likely to cause long-term environmental risk
- Estimate from reported literature values the concentration factors for each pollutant. These values for concentration factors will be expressed as the percent uptake-retention

and are calculated based on reported concentrations in both the donor and recipient compartments.

#### 4.3.1 Ecological Overview

In this portion of the study, the potential or final distribution of pollutants within a generic ecosystem has been investigated. The hypothetical temperate ecosystem chosen can be found in northern Appalachian and midwestern regions (Figure 4-4). The ecosystem is composed of both terrestrial and aquatic components, with biotic functional groups being specified for each compartment (i.e., producers, herbivores, omnivores, carnivores, and decomposers). Literature values pertaining to the abiotic components (soil, sediment, surface water, and groundwater) and functional groups likely to be found in the zone demarcated in Figure 4-4 were used in determining ultimate projected distribution.

This generic ecosystem has been partitioned into functional compartments which represent the dominant sinks, biotic groups, and pathways of a typical ecosystem. Figure 4-5 is a fifteen-compartment model of the hypothetical system under consideration. This diagram allows one to conceptualize more easily the number of sources that may influence a specific compartment's concentration and their complex interactions. Here a semantic difficulty needs clarification. If an organism magnifies a pollutant, its concentration on a per gram basis is greater than any of its source compartments. The term "magnify" is non-source specific and includes both food sources and abiotic exposure. For this discussion, this has been designated as ecomagnification or eco-accumulation. The classical terminology, in contrast, has been "biomagnification", based on the assumption that higher concentrations in the recipient organism result from food source ingestion only. This assumption disregards the abiotic exposure via inhalation, adsorption, or immersion. Therefore, in this presentation, ecomagnification is used and is based on all potential exposure modes within the ecosystem.

An alternate method of expressing the interactions of biotic and abiotic components in an ecosystem is shown in Figure 4-6. This matrix form of interactive notation lends itself to rigorous linear mathematical analysis and leads to defining the transient or time-based behavior of an individual

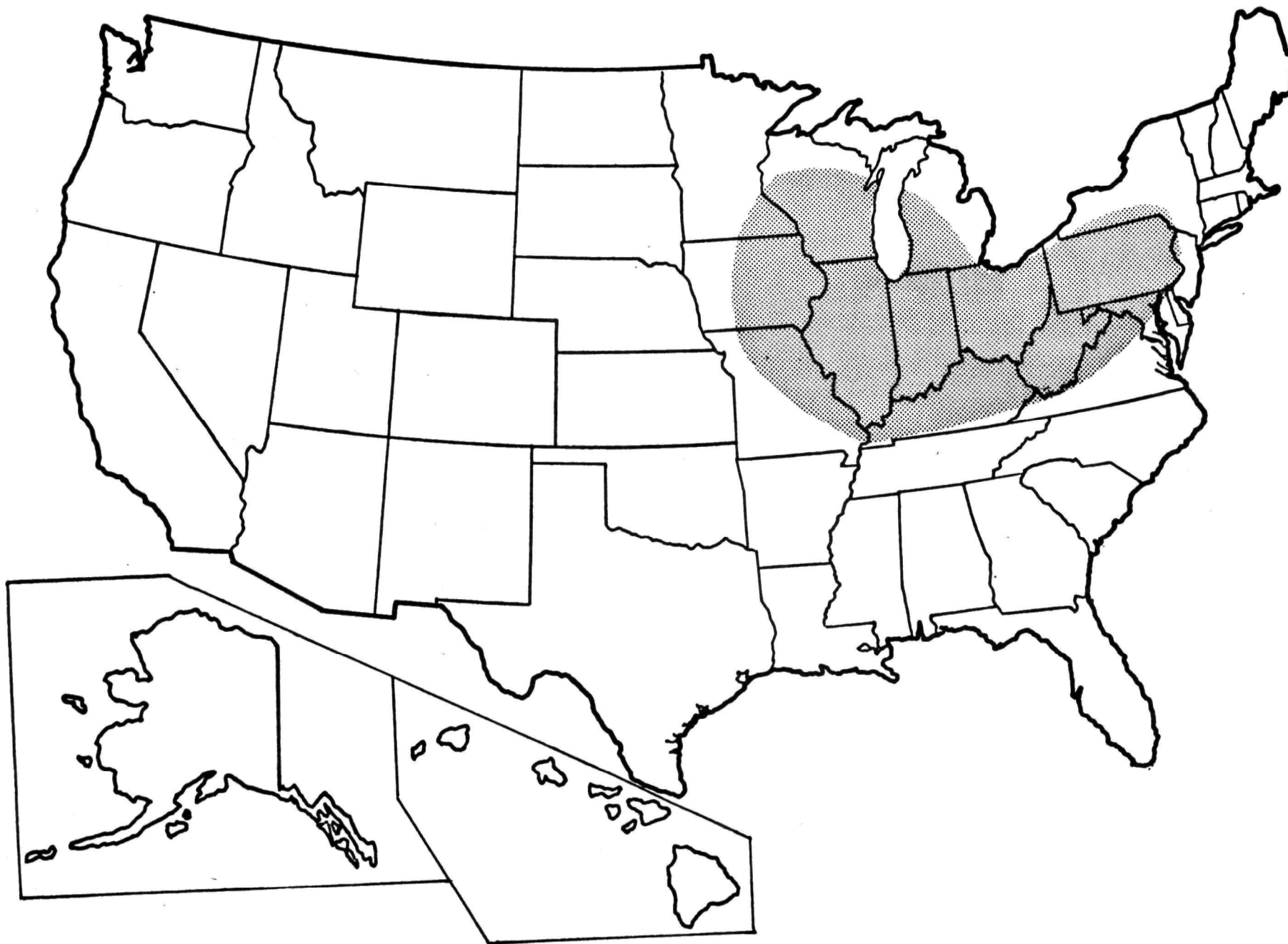
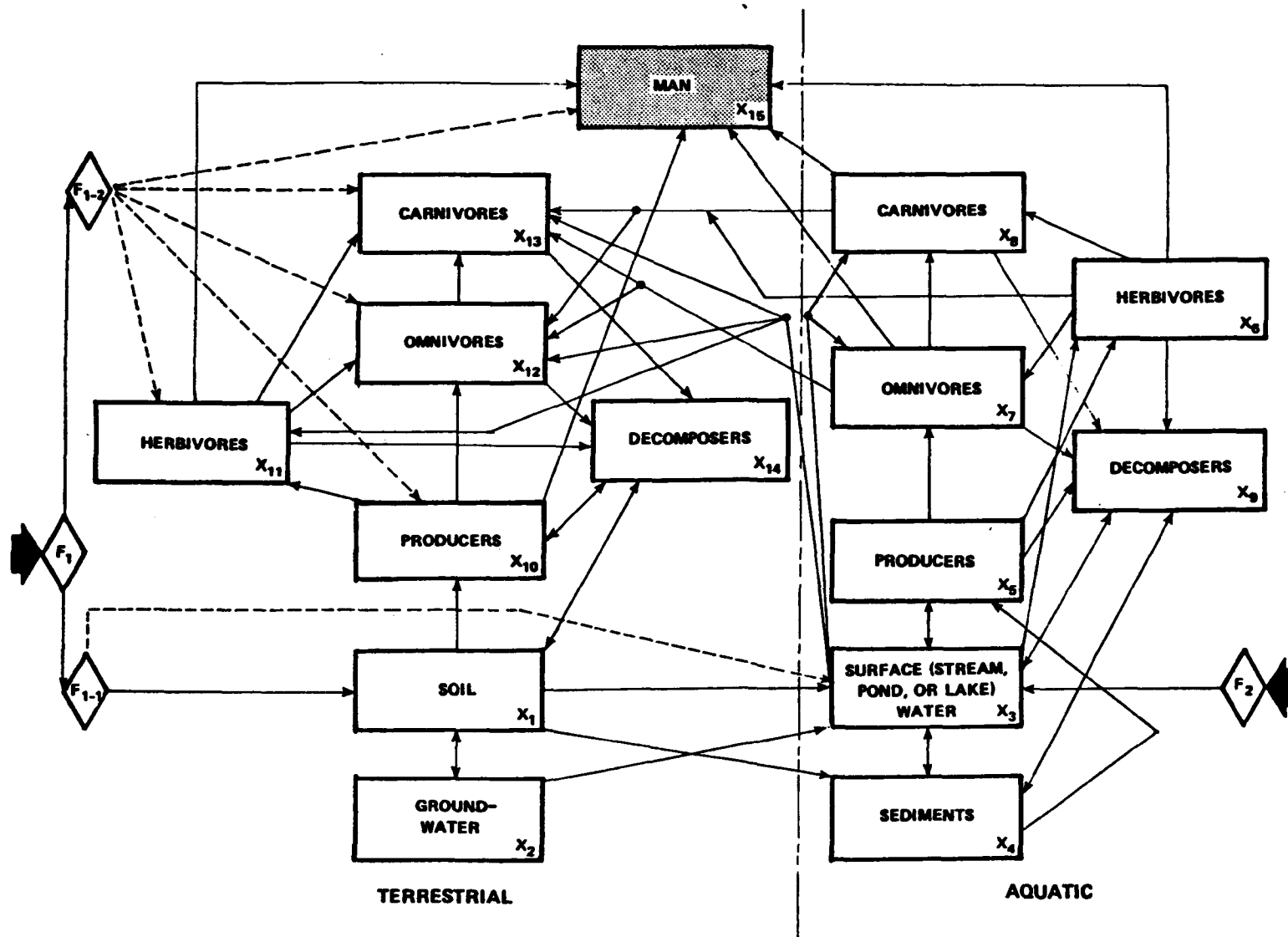


FIGURE 4-4. GENERAL AREA FOR WHICH GENERIC ECOSYSTEM IS DEFINED FOR PURPOSES OF ESTIMATING DISTRIBUTION OF POTENTIAL COAL CLEANING POLLUTANTS



[ $F_1$  (having components  $F_{1-1}$  and  $F_{1-2}$ ) = airborne atmospheric forcing function, and  $F_2$  = aquatic input forcing function.] Man is shown, but no data are reported.

FIGURE 4-5. COMPARTMENTAL MODEL OF GENERIC ECOSYSTEM AND DOMINANT PATHWAYS OF POLLUTANT TRANSPORT

		Biological Transport															
		Abiotic Components				Aquatic Components					Terrestrial Components					MAN	
		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X <sub>9</sub>	X <sub>10</sub>	X <sub>11</sub>	X <sub>12</sub>	X <sub>13</sub>	X <sub>14</sub>	X <sub>15</sub>	
Physical Transport	Abiotic Components	Soil X <sub>1</sub>	●	(b)												●	
		Groundwater X <sub>2</sub>	●														
		Surface Water X <sub>3</sub>	●	●		●					●						
		Sediments X <sub>4</sub>			●						●						
Biological Transport	Aquatic Components	Producers X <sub>5</sub>			●	●											
		Herbivores X <sub>6</sub>			●	(a)	●										
		Omnivores X <sub>7</sub>			●	(a)	●	●									
		Carnivores X <sub>8</sub>			●	(a)		●	●								
		Decomposers X <sub>9</sub>			●	●	●	●	●								
	Terrestrial Components	Producers X <sub>10</sub>	●									●					●
		Herbivores X <sub>11</sub>	(a)		(c)							●	●				
		Omnivores X <sub>12</sub>	(a)		(c)			●	●	●		●	●	●			
		Carnivores X <sub>13</sub>	(a)		(c)			●	●	●			●	●	●		
		Decomposers X <sub>14</sub>	●									●	●	●	●	●	
MAN X <sub>15</sub>			(d)	(d)			●	●	●		●	●					

(a) Indirect ingestion resulting from feeding habits.

(b) Irrigation, nominal in areas of groundwater irrigation.

(c) Surface water intake.

(d) Drinking water intake.

● Dominant system transfer.

Column element is the donor compartment and the row element is the recipient. but no data are reported.

MATRIX CONFIGURATION OF IMPORTANT RATE TRANSFER COEFFICIENTS WITHIN THE GENERIC ECOSYSTEM



component or of the entire system. This can be done by expressing the solution to each compartment's interactions as a differential equation with respect to time. For example, the rate of change of a pollutant concentration  $X_8$  in compartment 8, the aquatic carnivore, is given by:

$$\begin{aligned} \frac{dX_8}{dt} = & a_{3-8}X_3 + a_{6-8}X_6 + a_{7-8}X_7 - a_{9-8}X_9 - a_{12-8}X_{12} \\ & - a_{13-8}X_{13} - a_{15-8}X_{15} \end{aligned}$$

where  $X_8$  is the pollutant concentration in compartment 8,  $a_{i-8}$  represents the rate transfer coefficients for compartment  $i$  to compartment 8, and  $X_i$  is the pollutant concentration in compartment  $i$ , where  $i = 3, 6, 7, 9, 12, 13$ , or  $15$ . Therefore, compartmental values of pollutant concentration transient behavior could be predicted if and only if these transfer coefficients could be defined. The current state-of-the-art of research pertaining to the designated Priority 1 pollutants and their movement does not yet lend itself to accurate analysis of this nature.

#### 4.3.2 Pollutant Transfer

During coal cleaning, some contaminants are released and dispersed in the aquatic and terrestrial environments by means of atmospheric and aqueous inputs from refuse and coal storage areas, emissions from thermal dryers, waste water discharge, etc. However, long-term ecological behavior of trace elements in the biosphere including pathways, rates of dispersion, residence times in various components of the ecosystem, and chemical transformations, is largely unknown. Of the Priority 1 pollutants, cadmium, lead, and mercury represent the most heavily studied. Despite this, information relative to their rate of ecological transport is scarce. Cycling of heavy metals--their accumulation and transfer from water to man through the food chain--often can be brief and potentially dangerous. In addition, harmful effects on members of ecosystems usually have an indirect impact on man. For example, Truhart<sup>(17)</sup> notes:

- (1) Food resources are directly affected by immense fish kills caused by industrial discharge containing toxic

materials into rivers or lakes, or by the havoc wrought to agricultural crops by air pollution.

- (2) Agricultural productivity is indirectly affected by assaults on organisms that have a beneficial function in the biosphere, such as bees as vehicles for pollen, or earthworms and other organisms that ensure aeration of the soil medium.
- (3) Production of primary source materials, such as textile-producing plants and forest cultures, is affected by industrial discharge.
- (4) Toxicification of certain constituents of the food chain results in effects such as the toxicification of fish and the passage of various residues into milk. The presence of trace amounts of toxic organic contaminants in drinking water produced from contaminated river water can pose problems of the same magnitude.
- (5) The disturbance of biological balance or ecological stability can result in disastrous consequences on the regenerative capacities of the ecosystem and, as a result, the quality of life as a whole.

Iron, manganese, and selenium are essential elements for biological activities; however, excessive concentrations have been found to be toxic. Thus, there is a very delicate balance between the utilization of metals for important catalytic processes which occur in cells of organisms and the eco-accumulation of metals to a level that may be toxic to the cell. The accumulation of heavy metals by organisms is governed by many physiological and environmental factors, many of which are still unknown. Their toxicity and tolerance is equally complex.

4.3.2.1 Pollutant Uptake in Plants. Terrestrial autotrophs absorb pollutants via their roots from soil solution and direct adsorption of atmospheric particles deposited on leaf tissues. Aquatic plants, in addition to root uptake, absorb pollutants directly from the surrounding water. The availability and movement of elements and pollutants from soils and water to plants are not completely understood. Both direct ion

absorption and uptake of organic complexes are involved. Various conditions and factors influence the uptake of trace elements by plants. These include:

- (1) Chemical form of the pollutant
- (2) Concentration of the pollutant in soil or water
- (3) Interactions with other trace elements
- (4) Genetic constitution of the plant species
- (5) Solubility of the pollutant compound
- (6) Climatic conditions
- (7) Soil characteristics (e.g., pH, texture, till, composition, and structure)
- (8) Cation exchange capabilities of the soil.

The most important condition to consider in determining plant uptake is the availability of the trace element to the plant. Some soils may contain high concentrations of pollutants, but transport into plant tissues may be low due to the pollutants' unavailability. Soils high in organic matter or clay particles have an affinity for or the ability to retain large quantities of heavy metals. This decreases the availability of the heavy metals for plant uptake. In contrast, sandy soils have a lower capacity to retain heavy metals. This translates into a greater available concentration for plant uptake. On the other hand, leachability of heavy metals in sandy soils is greater, therefore reducing the amount available for plant uptake. These and other factors listed above, to a greater or lesser extent, influence the availability of trace elements and other pollutants for plant uptake.

4.3.2.2 Pollutant Uptake/Retention in Animals. Pollutants are absorbed by animals in one or more of the following ways: inhalation through the lungs, ingestion through the gastrointestinal tract, direct absorption through the skin or gills, fetal transfer through the placenta, and ovarian transfer into the egg. The percent uptake/retention in animals depends on several factors. These include:

- (1) Chemical form of the pollutant
- (2) Genetic constitution of the animal species
- (3) Concentration of the pollutant consumed or inhaled

- (4) Interactions with other trace elements, such as competitive antagonism among elements with similar properties and synergistic interactions
- (5) Element content in the gastrointestinal tract, such as in chelated or complexed formations, and in adsorption on surfaces of insoluble compounds
- (6) Feeding behavior of the animal.

Biological transformation can alter the pollutant either by synthesis or degradation into a form that is more or less available or toxic than the original form. A noteworthy example of biotransformation is shown in Figure 4-7 for mercury. In this case, both physical and biological forces change the form of mercury. In addition, it has been shown that inorganic mercury can be methylated in bottom sediments contained in fresh water aquaria to form both mono- and dimethylmercury. It is believed that this conversion involves anaerobic microbes. Thus, the relatively nontoxic inorganic and arylmercurials can be biologically converted to the extremely toxic methylmercury.<sup>(18)</sup> The pollutant, in various forms, is released into the environment from the animal by excretion (urine, feces, or volatilization from the body surface) and by decomposition after the animal's death. Three mechanisms that are important in the metabolism of a pollutant in an animal's body are transport, tissue retention, and excretion. These mechanisms are responsible for the length of time a pollutant remains in the body. Various pollutants also are retained in specific tissues in the body; this is evidenced by mercury and cadmium in the liver and kidney and by lead in bones.

4.3.2.3 Ecological Accumulation and Magnification. Those trace elements whose concentrations are higher in herbivorous animals than in plants, higher in omnivorous animals than in herbivores, and highest of all in top carnivores are said to be ecologically magnified or "accumulated in food chains". However, these terms, frequently misunderstood, present a misleading impression of simplicity of these mechanisms. The phenomenon of eco-accumulation, in fact, is quite complex. The ability of plants to concentrate metal ions is minimized by a number of factors; ion inactivation, soil fixation, accumulation at the soil surface above the root zone,

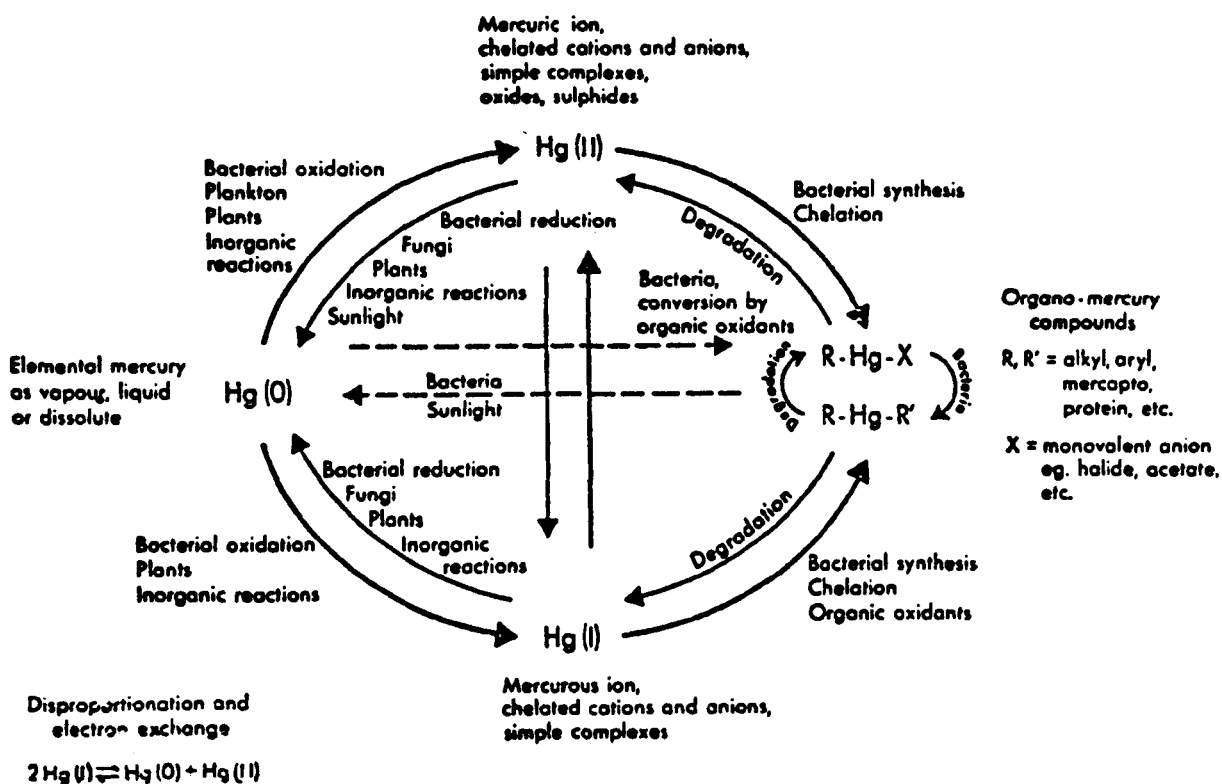


FIGURE 4-7. MERCURY INTERCONVERSIONS IN THE ENVIRONMENT<sup>(18)</sup>

Reprinted with permission from  
Jonasson, I.R., and Boyle, R.W.,  
"Geochemistry of Mercury", Proc.  
Soc. Can. Symp., Mercury in Man's  
Environment, Ottawa, February 15-16,  
1971, p. 5-21.

exclusion at the root zone, and immobility in the root.<sup>(19)</sup> The term accumulation refers to the greater trace metal concentration in the plant (recipient) than in the growth medium (donor).

Terrestrial animals ingest trace contaminants primarily through their food, or as a result of certain feeding habits, and by inhalation. Aquatic organisms, such as fish and crustaceans, absorb trace contaminants both from food and directly from the water in which they are immersed. Aquatic organisms must process large volumes of water to obtain oxygen so that water becomes their main route of exposure to toxic materials. Thus, for aquatic organisms, with the uptake/retention of a pollutant being primarily from ambient water, there is greater likelihood for eco-accumulation than in terrestrial organisms, where exposure to pollutants originates primarily with food sources. However, ecomagnification for terrestrial organisms does occur (e.g., for mercury and DDT).

According to the equilibrium theory<sup>(20)</sup>, organisms exposed to constant levels of toxicants display a rapid initial increase in the concentrations, which then level off to reach a quasi-equilibrium value. At this concentration, the rate of toxicant intake is balanced by the rates of excretion and metabolic breakdown. The lower the rate of excretion, the longer it takes to reach equilibrium and the higher the ultimate tissue concentrations. In general, larger animals have more difficulty excreting toxicants due to a lower metabolic rate and a smaller surface-to-volume ratio. Since predators are usually larger than their prey, a greater concentration can be expected in the predator. The equilibrium theory has been questioned since most animals in their natural environment are usually not exposed to a constant level of pollutant. This is due to the fact that environmental pollutants are not homogeneously distributed in the environment. However, pollutants tend to accumulate in biologically productive areas; thus predators, which usually concentrate their activities in such areas, can be exposed to high levels of pollutants.

In the past, there has been much controversy and confusion involving the term magnification. References to biomagnification through a food web seem to leave the impression that the toxicant is transferred solely through food sources. Thus, the focal point of the confusion is the exposure source. It is virtually impossible to delineate between the two

routes of exposure in the real environment. Huckabee<sup>(21)</sup> agrees with the general feeling that methyl mercury is biomagnified in terrestrial ecosystems; however, he argues with Goldwater's<sup>(22)</sup> and Peakall and Lovett's<sup>(23)</sup> contention that mercury biomagnifies in the aquatic ecosystem. Here we avoid the argument by defining the term as ecomagnification, which includes all sources of exposure. It then becomes clear that ecological magnification of toxic materials is a phenomenon controlled by numerous ecological variables, in addition to physiological and physico-chemical factors.

#### 4.3.3 Designated Priority 1 Pollutants

The review of the literature has been limited to those references dealing with movement of Priority 1 pollutants for which percent uptake/retention (on a concentration basis) could be calculated. Information extracted from these references is listed in Tables 4-1 through 4-8 for each of the eight elements investigated. The tables are arranged according to the individual pollutant, and within each table entries are classified according to the functional component (i.e., abiotic component, terrestrial producers, terrestrial herbivores, etc.). Functional components lacking representative samples were omitted. Listed for each entry are the sample type, source form, percent uptake/retention, additional remarks, and reference. The sample types are listed by common name, but the scientific name is listed when given in the reference.

As stated previously, the chemical form of the pollutant in question is of paramount importance when dealing with ecological transport and fate problems. In the following narrative sections and tables dealing with the ecological distribution of Priority 1 pollutants, it may seem as if the reference is to the elemental form of that pollutant; however, it should be recognized that an unspecified form of that pollutant is being referred to. For example, mercury-contaminated fly ash used in plant uptake experiments or discussion of the toxic effects of beryllium do not necessarily refer to the elemental form of these metals, but rather to an unspecified chemical form of the pollutant in question.

Calculation of values for percent uptake on the basis of concentration required specific pieces of information. Plant uptake values were calculated by dividing the concentration of pollutant in the plant by the concentration of pollutant in the soil and nutrient solution. For example, 5 ppm cadmium is present in the soil and 2.5 ppm cadmium is present in an oak tree grown in the contaminated soil; therefore, the percent uptake on a concentration basis is 50 percent. Animal uptake values were calculated in a similar manner by dividing the concentration of pollutant in the recipient by the concentration of pollutant in the food source, water, or gas to which the animal was exposed. The percent uptake values are recorded as single values, range values, or a mean value  $\pm$  the standard deviation. Similar values recorded as concentration factors are most common in the literature; however, for purposes of these tables, the values have been recorded as percent uptake/retention. The percent uptake/retention is equal to the concentration factor times 100.

In addition, such information as type of experiment, mode of administration or application, time period, soil characteristics and/or tissue concentration sampled have been presented as remarks when available or pertinent. Identifying the type of experiment, either field, laboratory, or microcosm, can be extremely important when interpreting the percent uptake values. In a microcosm study by Huckabee and Blaylock<sup>(24)</sup>, a radioisotope was applied to a model ecosystem. At the termination of the experiment a materials balance was performed to identify target organisms and sinks. Studies of this type identifying total distribution of a pollutant within an ecosystem are highly desirable but are extremely scarce. Microcosm studies should be interpreted from an overall systems view. Laboratory experiments<sup>(25,26,27)</sup>, on the other hand, are usually based on response of an individual organism to a pollutant. That is, a laboratory animal is given a contaminated food and after a period of time is analyzed to determine the pollutant concentration. This type of study examines an individual's metabolism of the pollutant while the microcosm study examines the system's metabolism of the pollutant. In field experiments, percent uptake values are determined from resident pollutant concentrations present in the environment and biota<sup>(28,29)</sup> or by spiking the ecosystem with known concentrations of pollutants and determining concentrations in each



compartment.<sup>(30,31,32)</sup> Information presented as representing standing pool values was of little use for calculating percent uptake on a concentration basis in this study. Standing pools of toxicants are represented as the total amount in any of the ecological compartments (i.e., biomass x concentration).

It should be emphasized that since the conditions and methods are quite different for each experiment type, differences in calculated percent uptake values can be expected. The tables are not intended to represent accurate uptake values, but rather are to be used for identifying concentration and/or expected magnification within the functional components of a generic ecosystem of Priority 1 pollutants.

4.3.3.1 Arsenic. Arsenic appears in Group V of the Periodic Table of Elements which also includes nitrogen, phosphorus, antimony, and bismuth. Although it is strictly a nonmetal or metalloid, the element in one free form is commonly referred to as "arsenic metal". It usually occurs in small quantities in association with other metals and in crystalline rocks, schists, and coals. Therefore, it is considered as a potential pollutant in association with the coal cleaning process. The most prevalent chemical forms are the oxides, arsenates, sulfides, and complexes with other metals.

Research work over the past century has clearly demonstrated that arsenic is toxic when received either as an inhalant or through food source contamination.<sup>(33)</sup> Most reports have dealt solely with acute exposures from industries that manufacture products containing high levels of arsenic (certain war gases or pesticides) rather than chronic (low level) exposures that one might anticipate from a coal cleaning facility. This makes references related to arsenic movement within ecosystems usually unavailable because research has concentrated on the chemical form of input, its transition chemistry, toxicity, and the analytical methods.

The toxicity of the most common inorganic arsenic form, a + 3 valence, varies widely, as reported by Schroeder and Balassa.<sup>(34)</sup> Bacteria have been toxified with as low as 290 ppm and as high as >10,000 ppm, whereas rats and mice have been found to have LD<sub>50</sub> concentrations ranging from 5.8 ppm to 21.0 ppm. The phenomenon of decreasing toxicity as one moves closer

to the more rudimentary or fundamental single cellular organisms is not uncommon in environmental toxicology. Thus, prediction of effective concentrations (EC) or permissible release rates is difficult and usually inaccurate.

Bio-accumulation of arsenical pesticides has been noted by Woolson.<sup>(35)</sup> Luh, et al.,<sup>(36)</sup> also report bio-magnification to be evident in aquatic food webs. However, the same argument is posed for arsenic as for all other Priority 1 pollutants; that is, it has not been clearly demonstrated whether the increasing concentrations of toxicants as one moves through the food web result from abiotic exposure or from actual biological ingestion.

Table 4-1 presents the best available data as it relates to anticipated distribution of arsenic in a typical generic ecosystem as so defined.

4.3.3.2 Beryllium. There is a strong contrast between the toxic effects of beryllium released as a result of industrial activities and the lack of harmful effects of beryllium in natural materials. Beryllium is widespread in the rocks of the earth's crust and in soils derived from them. The concentration of beryllium in soils in the United States ranges from less than 1 up to 7 ppm, with a mean value of approximately 1 ppm. Areas rich in beryllium are small and usually located away from areas important in food production. Very little beryllium is released to groundwater during weathering because of prompt capture by clay particles. The concentrations in surface waters of the eastern U.S. range from 0.1 to 0.9 ppb.<sup>(37)</sup> But beryllium has been found in coal ash, originating primarily from the organic matter of the coal, in concentrations as high as 100 ppm.

The toxic effects of beryllium have been documented<sup>(27,38)</sup>; however, very little information exists on its uptake by plants and animals. The major potential toxic hazard to humans is via the inhalation of beryllium-containing fumes and dusts that might emanate during processing operations.<sup>(39)</sup> Inhaled beryllium concentrates in the skeletal system and lungs depending on the compound.<sup>(40)</sup> However, the highest beryllium concentrations are usually associated with the liver, spleen, and bone marrow.<sup>(41)</sup>

An inhibiting effect of beryllium on the growth of bush beans was evident from the dry weight of the plants grown in beryllium solutions of

TABLE 4-1. VALUES FOR ARSENIC UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Abiotic Components</u>				
Soil	Pentavalent <sup>74</sup> As in soil	66.2-97.1	Microcosm	42
Water	<sup>74</sup> As in water	14.5-16.4	Microcosm (sediment)	43
Water	Arsenic** in water	5.0	Field (New Zealand)	44
Water	Arsenic**	1.2	Field (Newfoundland)	45
Water	AsSO <sub>3</sub> in solution	10.0	Field experiment (30 days)	46
Sediment	AsSO <sub>3</sub> in solution	87.0	Field experiment (30 days)	46
Sediment	Arsenic**	96.0	Field (Newfoundland)	45
<u>Terrestrial Producers</u>				
Grass (mixture)	Arsenate in solution	2.14	Field (natural background study)	34
Ferns	Arsenate in water	12.31	Field (natural background study)	34
Pine needles	Arsenate in soil	8.79	Field (natural background study)	34
Agricultural crops	Arsenic pesticides in soil	16.0-0.10	Field	47
Agricultural crops	Arsenic pesticides in soil	0.83	Field	48
Agricultural crops	Arsenic pesticides in soil	1.25	Field	49

\*On a concentration basis.

\*\*Chemical form not specified.

TABLE 4-1. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Aquatic Producers</u>				
Benthic algae	Potassium arsenate Sodium arsenate	200	Field	36
Algae	<sup>14</sup> C-Cacodylic acid	450	Microcosm	50
Algae	Arsenic** in water	3400	Microcosm (model ecosystem)	35
<u>Aquatic Herbivores</u>				
Mollusks	Potassium arsenate Sodium arsenate in water	650	Field	36
Snails and daphnia	<sup>14</sup> C-Cacodylic acid	44-86	Microcosm	50
Daphnids	Arsenic** in water	40-50	Microcosm (model ecosystem)	35
<u>Aquatic Omnivores</u>				
Fish	<sup>14</sup> C-Cacodylic acid in water	3.1-5.7	Microcosm	50
Crustacean and fish	Potassium arsenate Sodium arsenate in water	400-700	Field	36

\* On a concentration basis.

\*\* Chemical form not specified.

various concentrations.<sup>(51)</sup> Beryllium might also be injurious to higher plants if high levels were dispersed onto soil or into ground and irrigation waters where plant roots might come in contact with beryllium concentrations exceeding 1 ppm. Studies by Slonim indicated that the amount of beryllium concentrated within the bodies of guppies (Lebistes reticulatus) varied directly with the concentration of beryllium in the surrounding medium and to a lesser extent with the exposure period.<sup>(27)</sup> In general, Slonim's results indicate that toxicity and lethality may depend on the amount of beryllium concentrated within the fish but would more likely be due to the effect of beryllium on a particular target organ or cellular or subcellular component.

According to the data presented in Table 4-2, beryllium accumulates to a considerable degree in various vegetable crops and in the aquatic omnivore, Lebistes reticulatus. Beryllium concentrations were noted to be highest in the root zone of vegetable crops and in the gastro-intestinal tracts, kidneys, and ovaries of aquatic omnivores. There can be no conclusion drawn on the ecological magnification of beryllium in either aquatic or terrestrial ecosystems; however, the existing data imply that beryllium concentrations in plants and animals can be greater than those in the medium.

4.3.3.3 Cadmium. Cadmium may be considered as one of the rarer elements found naturally in the earth's crust; however, it is fairly accessible mainly as an industrial by-product. Cadmium, which is always found in association with zinc, is released as a result of zinc smelting operations and electrolytic refining. Many of the forms of cadmium released as a result of these processes are soluble and biologically active; therefore, they pose a serious, potential source for organism contamination.<sup>(52)</sup> Zinc is an essential element for biological processes while cadmium is not. Concern about environmental contamination from cadmium stems from the metal's known tendency to replace zinc in certain enzymes, thereby altering their stereostructure, impairing their catalytic activity, and causing disease.<sup>(28)</sup> Cadmium is present in various quantities in soil, water, air, and food. In non-polluted areas, the concentration of cadmium is reported to be <1 ppm in soil and <1 ppb in water.

TABLE 4-2. VALUES FOR BERYLLIUM UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Producers</u>				
Alfalfa	BeCl <sub>2</sub> in nutrient solution	$1.93 \times 10^2 \pm 0.72 \times 10^2$	Leaf and stem concentrations	53
Barley	BeCl <sub>2</sub> in nutrient solution	$3.50 \times 10^2 \pm 0.91 \times 10^2$ $1.29 \times 10^4 \pm 0.57 \times 10^4$	Foliage concentration Root concentration	53
Pea	BeCl <sub>2</sub> in nutrient solution	$5.48 \times 10^2 \pm 1.57 \times 10^2$	Leaf and stem concentrations	53
Lettuce	BeCl <sub>2</sub> in nutrient solution	$7.0 \times 10^2 \pm 3.80 \times 10^2$	Foliage concentration	53
Bush bean	Be in solution**	$4.08 \times 10^4 \pm 1.01 \times 10^4$ $6.46 \times 10^2 \pm 1.29 \times 10^2$ $15.4 \times 10^2 \pm 1.34 \times 10^2$ $1.77 \times 10^2 \pm 0.35 \times 10^2$	Root concentration Stem concentration Leaf concentration Fruit concentration	51
<u>Terrestrial Omnivores</u>				
Lab rat	<sup>7</sup> BeCl <sub>2</sub> in solution	< 0.2	Laboratory, administered by stomach tube	26
<u>Aquatic Omnivores</u>				
Guppy (Lebistes reticulatus)	<sup>7</sup> BeSO <sub>4</sub> in water	$1.216 \times 10^2 \pm 0.95 \times 10^2$	Laboratory	27

\* On a concentration basis.

\*\* Chemical form not specified.

There have been numerous studies documenting the toxicity of cadmium to plants and animals. However, there is little information in the literature related to the behavior of cadmium in ecosystems and to its transport through food webs. Cadmium is relatively immobile in both terrestrial and aquatic environments. According to the data presented in Table 4-3, the greatest proportion (98.9 percent) of the cadmium remains in the soil and litter, and of the cadmium introduced into the aquatic environment, 92 percent remains in the sediment. In ecosystems subject to various inputs of cadmium, those animals whose food base is in the soil and litter or detritus are most susceptible to contamination. The terrestrial decomposers, earthworms and woodlice, substantiate this susceptibility by displaying uptake values ranging from  $1.9 \times 10^2$  percent to  $1.74 \times 10^3$  percent. In addition, the crayfish whose food base is in the detritus also shows signs of ecological magnification of cadmium. However, this phenomenon is due solely to direct uptake from the water environment. Ecological magnification of cadmium in a grassland arthropod food chain does not occur.<sup>(52)</sup> Field crickets accumulated 60 percent of the cadmium concentration found in the contaminated vegetation and the predacious wolf spider accumulated only 70 percent of the cadmium found in the crickets. Ecological magnification of cadmium is evidenced in the aquatic environment. Martin<sup>(54)</sup> states that cadmium concentrations in zooplankton are more than 6000 times that in water. In addition, concentrations in algae are 100 to 1000 times that in water.<sup>(55)</sup>

As shown in Table 4-3, producers, in most cases, do not ecomagnify cadmium. Pollutant uptake by plants, as mentioned in a previous section, depends on many factors. In a radiotracer study of cadmium behavior in aquatic and terrestrial ecosystems, two chemical forms of cadmium were tested.<sup>(30)</sup> The water soluble  $\text{CdCl}_2$  was found to have a greater availability for uptake than the water insoluble  $\text{CdO}$ . Uptake of trace elements in soil by plants is highly dependent on the equilibrium of the chemical activity of cations in the soil solution. It is important to measure the free ion in solution to estimate availability. Cadmium uptake from soil by plants was found to be greater in acid soils and lower in organic soils than in mineral soils; however, organic acids from decaying leaf litter

TABLE 4-3. VALUES FOR CADMIUM UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Abiotic Components</u>				
Soil	$^{109}\text{CdCl}_2$ in solution	$98.9 \pm 1.2$	Field, spray application to clipped plot	56
	$^{109}\text{CdCl}_2$ in solution	$95.7 \pm 3.7$	Field, spray application to unclipped, vegetated plot	
	$^{115}\text{CdCl}_2$ in solution	85.5	Microcosm, applied as simulated rainfall, 27 days	24
	$\text{CdCl}_2$ in solution	$88.4 \pm 2.7$	Microcosm, applied as simulated rainfall, 70 days	57
	$^{109}\text{CdCl}_2$ in solution	91.2	Field, applied as simulated rainfall, 6 months	31
Sediment	$^{115}\text{CdCl}_2$ in solution	$92.47 \pm 1.82$	Microcosm, transport from a terrestrial microcosm, 27 days	24
Water	$^{115}\text{CdCl}_2$ in solution	$6.07 \pm 0.26$	Microcosm, transport from a terrestrial microcosm, 27 days	24
<u>Terrestrial Producers</u>				
Moss	$^{115}\text{CdCl}_2$ in solution	$9.2 \pm 1.4$	Microcosm, 27 days	24
Higher plants	$^{115}\text{CdCl}_2$ in solution	$0.20 \pm 0.14$	Microcosm, 27 days	24
Grass	Cd from automobile emissions in soil **	$127.0 \pm 33.0$	Field, soil pH 5.9	28
		$19.8 \pm 5.8$	Field, soil pH 7.1	
Grasses, forbes, and goldenrod	$^{109}\text{CdCl}_2$ in solution	$0.71 \pm 0.75$	Field, applied as simulated rainfall, clipped plots	31
		$3.25 \pm 1.82$	Field, applied as simulated rainfall, unclipped plots	

\* On a concentration basis.

\*\* Chemical form not specified.



TABLE 4-3. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
Old field vegetation	CdCl <sub>2</sub> in solution	2.0 ± 0.9	Field, spray application to clipped plots, 1 month	56
		6.9 ± 1.9	Field, spray application to unclipped plots, 1 month	
Vegetable crop	Cd in soil**	141.26 ± 24.0	Field	58
Soybean	<sup>115</sup> Cd in soil**	15.78	Field, root uptake from soil	59
	<sup>115</sup> Cd in solution**	1.93	Field, foliage application and uptake	
Oat shoots	Cd in soil**	34.8-41.3 39.2-66.2	Field, 46 ppm applied in soil Field, 1.3 ppm applied in soil	32
Wheat	Cd in soil**	167.9 ± 159.3	Field	60
Oak tree	Cd in litter-soil**	34.9 ± 0.5	Field	61
Sweet clover	Cd in fly ash**	25.4	Field	62
<u>Terrestrial Herbivores</u>				
Rabbit	Cd in iron dust**	~ 30.0	Laboratory, inhalation	63
Sheep	CdCl <sub>2</sub> in feed	5.3		64
Cow	CdCl <sub>2</sub> in feed	18.0		65
Goat	<sup>109</sup> CdCl <sub>2</sub> in feed	~ 2.0		66
Grasshopper	Cd in vegetation**	~ 130	Field	67

\* On a concentration basis.

\*\* Chemical form not specified.

TABLE 4-3. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Omnivores</u>				
Lab rat	$^{109}\text{CdCl}_2$ in solution	0.5-8	Orally administered, 4 hours	68
Lab rat	$^{115}\text{CdNO}_3$ in solution	1-2	Administered by stomach tube, 24 hours	69
Lab mouse	$\text{CdCl}_2$ in gaseous form	10-20	Inhalation	70
Lab mouse	$^{109}\text{Cd}$ **	0.5-3.0		71
Lab mouse	$^{109}\text{CdCl}_2$ in solution	4.5-12 1.0-2.3	Stomach injection, 11 hours Stomach injection, 164 hours	72
$\infty$ Lab mouse	$^{109}\text{CdCl}_2$ in solution	1.6	Orally administered, ~15 days	25
Lab mouse	$^{115}\text{CdCl}_2$ in solution	7.3 2.7	Orally administered, 24 hours Orally administered, 48 hours	73
Chipping sparrow	Wild bird seed soaked in $^{109}\text{Cd}$ solution **	8	Ingestion, 20 days	74
Field cricket	Vegetation grown in $^{109}\text{Cd}$ solution **	60.9	Ingestion, 30 days	52
<u>Terrestrial Carnivores</u>				
Dog	$\text{CdCl}_2$ in gaseous form	~ 40	Inhalation	75
Wolfe spider	Crickets fed on $^{109}\text{Cd}$ -grown vegetation **	71.4	Ingestion, 30 days	52
Predatory arthropod	Cd in prey **	$124.0 \pm 93.5$	Field, ingestion	76

\* On a concentration basis.

\*\* Chemical form not specified.

TABLE 4-3. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Decomposers</u>				
Earthworm	Cd in soil**	$1.74 \times 10^3 \pm 0.42 \times 10^3$	Microcosm	30
Earthworm	Cd in soil**	$1.03 \times 10^3 \pm 0.03 \times 10^3$		77
Earthworm	Cd in soil**	$1.63 \times 10^3$		78
Woodlouse	Cd in litter-soil**	$4.96 \times 10^2 \pm 1.90 \times 10^2$		54
Arthropod litter consumer	Cd in litter**	$36.8 \pm 18.4$		76
<u>Aquatic Producers</u>				
Watercress	$^{115}\text{CdCl}_2$ in water	< 2.06	Microcosm, 27 days	24
<u>Aquatic Omnivores</u>				
Snail (Goniobasis clavaeformis)	$^{115}\text{CdCl}_2$ in water	< 2.25	Microcosm, 27 days	24
Crayfish (Orconectes propinquus)	$^{109}\text{CdCl}_2$ in water	$1.84 \times 10^5$	Field	79
<u>Aquatic Carnivores</u>				
Fish (Gambusia affinis)	$^{115}\text{CdCl}_2$ in water	< 2.25	Microcosm, 27 days	24

\*On a concentration basis.

\*\*Chemical form not specified.

increases solubility and subsequent transport of heavy metals<sup>(80)</sup>. Data presented by Miller, et al.<sup>(81)</sup> show a cadmium uptake by corn plants higher than values reported in most literature. This may have been due to the low ion exchange capacity of the sandy loam soil used in the experiment. A change in soil pH from 5.9 to 7.1 decreased the percent cadmium uptake from 127 percent to 20 percent.<sup>(28)</sup> In the absence of iron chelates there was no difference between cadmium uptake from pH 4 and pH 6 soil solutions, while in the presence of Fe DTPA, plants grown in lower pH soil had a significantly greater uptake. Also, the addition of zinc to cadmium contaminated soils decreased the availability of cadmium for plant uptake.<sup>(82)</sup>

Cadmium is predominantly released from industrial activities as an atmospheric aerosol, with the airborne particulates containing cadmium being deposited on the surface of soils and plants by rain, snow, or as particulate fallout. In grain crops, cadmium absorption via the foliage from airborne particulates is not as serious as absorption via the root systems from contaminated soils.<sup>(59)</sup> However, it is important to remember that those crops consumed by either man or animals are continuously exposed directly to atmospheric contamination. Cadmium is absorbed and retained to a considerable degree in the body of animals following inhalation. The absorption is primarily directly from the lungs. Animal experiments have shown that absorption is between 10 and 40 percent of the inhaled cadmium. A considerable difference might well exist for different cadmium compounds.<sup>(83)</sup>

There are no clear indications from the data presented in the literature of any differences in the cadmium uptake of herbivorous and carnivorous animals. Body concentrations of cadmium are greatest in the liver and kidneys.<sup>(84)(74)</sup> Cadmium retention from gastrointestinal absorption is greater for acute doses than for chronic doses.<sup>(83)</sup> Dietary factors have been shown to influence uptake and retention of cadmium in animals. Laboratory rats on a low calcium diet accumulate 50 percent more cadmium than rats on a high calcium diet<sup>(85)</sup>. Mice on a low protein diet had higher levels of cadmium than mice on a high protein diet.<sup>(72)</sup> Cadmium will be found in blood, internal organs, and excreta after absorption following exposure via air, oral intake, or injection.

With increasing amounts of cadmium entering the biosphere, it is important to examine the uptake and elimination of this element in organisms

and to relate elemental cycling processes to food web dynamics. An understanding of these mechanisms would allow predictions of the concentrations of cadmium in the various ecological compartments.

4.3.3.4 Iron. Iron ranks second to aluminum in abundance in the earth's crust. Depending on the season, river water concentrations of iron may range up to several parts per million.<sup>(86)</sup> Iron exists in the environment in close association with sulfur. It is sufficiently stable to exist in the free state and its compounds may be in either of two oxidation states, both of which can form readily under natural conditions.

Iron is an essential element; it is vital for both plants and animals. In higher animals the blood pigment, hemoglobin, contains an iron complex. Iron may also be present in some enzymes. The iron bacteria (general Leptothrix, Gallionella, and Spirophyllum) accumulate ferric hydroxide in a sheath as a part of their cell structure. Phytoplankton exhibit a capacity to concentrate iron up to 100,000 times the concentration in water.<sup>(87)</sup> There are other species that have the ability to ecomagnify iron, but a true understanding of this system remains obscure.

Referring to Table 4-4, terrestrial plants and animals show very low percent uptake values; however, macrophytes and whitefish ecomagnify iron in the aquatic environment. Their most significant route for uptake seems to be by absorption from the water environment rather than transfer through food sources.

4.3.3.5 Lead. Large quantities of lead are used each year in the United States. The largest consumer is the electric-storage battery industry (39 percent), followed by the petroleum industry which uses 20 percent of the total for gasoline additives. The amount of lead released into the atmosphere over the United States is measured in hundreds of tons per day, of which 98 percent can be attributed to the combustion of gasoline. Since lead from automobile exhaust is an important source of lead contamination, many studies involve roadside ecosystems.<sup>(88,89,90,91)</sup> In addition, lead smelters have been investigated as a major contributor to environmental lead contamination.<sup>(54,76)</sup> The concentration of lead in the atmosphere is highly variable depending on vehicular density and climate. Much of

TABLE 4-4. VALUES FOR IRON UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Producers</u>				
Sweet Clover	Fe in fly ash **	0.51	Field	62
<u>Terrestrial Herbivores</u>				
Cotton rat	<sup>59</sup> Fe tagged lettuce**	1.5	Laboratory, absorbed in tissue after 15 hours	92
<u>Terrestrial Carnivores</u>				
Assassin bug (Triatomid)	<sup>59</sup> Fe in hemoglobin injected in chicken**	~2.0-3.0	Laboratory, 87 days (blood sucking and/or insectivorous)	93
<u>Aquatic Producers</u>				
Macrophyte	Fe in water**	$3.6 \times 10^5$ <sup>+</sup> (wet weight) $2.3 \times 10^5$	Field	29
<u>Aquatic Carnivores</u>				
Whitefish	Fe in water**	$1.4 \times 10^4$ (wet weight) $1.5 \times 10^5$ (wet weight)	Field, muscle concentration Field, bone concentration	29

\* On a concentration basis.

\*\* Chemical form not specified.

the lead in the air is removed by aggregation and precipitation. The usual range of lead in soils is from 2 to 200 ppm.<sup>(94)</sup> A majority of the lead in the aquatic ecosystem is insoluble and apparently ends up in the sediments.

Soil lead is largely unavailable for uptake by plants; only 0.003-0.005 percent of the total lead in soil is available for such uptake.<sup>(84)</sup> Lead can be accumulated in plants from air and soil, but it rarely ecomagnifies. In an exception to the rule, however, fungi in a laboratory experiment concentrated lead at 34 times the concentration in the culture medium.<sup>(95)</sup> A majority of the lead deposited on vegetation from the atmosphere can be removed by washing<sup>(96)</sup>. Translocation of lead from the roots is highly variable depending on soil characteristics and plant species<sup>(97)</sup>. Most of the lead seems to accumulate in the root system, with significantly lower levels in the stems and leaves.<sup>(98)</sup> The edible portion of exposed vegetable plants contains only slightly more lead than control plants, but the non-edible portion contains 2 to 3 times as much lead<sup>(99)</sup>. The formation of organic chelates may make lead more mobile in the soil but less available to plants.<sup>(100)</sup> The level of available phosphorus in the soil also affects lead uptake in a variety of plants<sup>(98)</sup>.

Lead is a non-essential, cumulative element, which is stored mainly in the bones and kidneys.<sup>(94)</sup> A low intestinal absorption (less than 5 percent) was noted in cattle six days after ingestion of lead-203 spiked grain feed.<sup>(101)</sup> In a study involving levels of lead in roadside animals, inhalation of lead sorbed on particles was demonstrated to be another important avenue of intake.<sup>(93)</sup> Even though high concentrations of lead are retained in the soil (97 percent), soil decomposers, such as the earthworm and arthropod litter consumers, do not ecomagnify lead (Table 4-5). However, lead is ecomagnified from the herbivore to carnivore-trophic level in arthropod food webs.<sup>(102,76)</sup> In the vicinity of lead mining and milling operations in Missouri, there was no magnification of lead found in the grazing food chains involving aquatic vegetation heavily laden with lead.<sup>(103)</sup> Leland and McNurney<sup>(104)</sup>, in a study on distribution and bioaccumulation of lead in a river ecosystem, found higher lead concentrations in detrital feeders and herbivores than carnivores. Aquatic

TABLE 4-5. VALUES FOR LEAD UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Abiotic Components</u>				
Soil	Pb in aqueous slurry**	~ 97.0	Microcosm	105
<u>Terrestrial Producers</u>				
Lichens	Pb in soil**	4.0	Laboratory, soil concentration - 27,500 ppm	106
		125.0	Laboratory, soil concentration - 20 ppm	
Fungi	Pb in culture median**	$3.4 \times 10^3$	Laboratory	95
Vegetable crop	Pb in soil**	$31.49 \pm 52.32$	Field	58
Corn	PbCl <sub>2</sub> in soil	45.0		107
Soybean	PbCl <sub>2</sub> in soil	15.1		107
Lettuce	Pb(NO <sub>3</sub> ) <sub>2</sub> in soil	10.9		96
Lettuce	PbCl <sub>2</sub> in soil	14.1		108
Oats	Pb(NO <sub>3</sub> ) <sub>2</sub> in soil	4.0	Shoots	96
		11.4	Roots	
Oats	PbCl <sub>2</sub> in soil	5.7	Tops	108

\* On a concentration basis.

\*\* Chemical form not specified.



TABLE 4-5. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Omnivores</u>				
Cattle	$^{203}\text{Pb}$ in feed**	< 5.0	6 days	101
<u>Terrestrial Carnivores</u>				
Predatory arthropod	Pb in prey**	$116.0 \pm 29.0$	Field, ingestion	76
<u>Terrestrial Decomposers</u>				
Earthworm	Pb in soil**	17.4		56
Earthworm	Pb in soil**	$95.0 \pm 25.0$		77
5 Woodlouse	Pb in litter-soil**	$60.0 \pm 14.8$		54
Arthropod litter consumer consumer	Pb in litter**	$7.0 \pm 2.0$		76
<u>Aquatic Producers</u>				
Bulrush ( <i>Scirpus americanus</i> )	Pb in solution**	$3.6 \times 10^3$ $5.9 \times 10^4$	Stem, laboratory rhizome	109
Spike rush ( <i>Eleocharis smallii</i> )	Pb in solution**	$2.3 \times 10^4$ $2.2 \times 10^5$	Stem, laboratory rhizome	109
Pitchforks ( <i>Bidens cernera</i> )	Pb in solution**	$9.3 \times 10^3$ $4.2 \times 10^4$	Stem, laboratory rhizome	109
<u>Aquatic Herbivores</u>				
Mayfly	$\text{Pb}(\text{NO}_3)_2$ in solution	$11.82 \times 10^5 \pm 2.57 \times 10^5$	Laboratory	110
<u>Aquatic Omnivores</u>				
Stonefly	$\text{Pb}(\text{NO}_3)_2$ in solution	$4.29 \times 10^4 \pm 1.39 \times 10^4$	Laboratory	110

\* On a concentration basis.

\*\* Chemical form not specified.

organisms display ecomagnification of lead in solution; however, the occurrence of this phenomenon is most likely due to direct uptake of lead in solution and not to transfer in the food web.

4.3.3.6 Manganese. Manganese, the twelfth most abundant element, constitutes about 0.10 percent of the earth's crust.<sup>(111)</sup> Manganese is next to iron in the periodic series, similar to it in its chemical behavior, and often closely associated with it in its natural occurrence. Total manganese in the soil ranges from <1 ppm to 7000 ppm with a geometric mean of 340 ppm<sup>(112)</sup>. Manganese in soils reflects the influence of rock sources as soil parent materials and the nature of unconsolidated deposits on which soils are formed, as well as manganese losses through soil weathering. The manganese content of groundwater ranges from <0.01 ppm to 0.87 ppm<sup>(113)</sup> and natural waters generally contain 0.2 ppm or less.<sup>(114)</sup>

Manganese deficiencies and toxicities are well documented for a wide range of plants<sup>(115)</sup>; however, data dealing with percent uptake and ecological transport are scarce. Manganese in the ecosystem has well established lines of movement from rocks to soils to plants to animals, from soils to water, to organisms and back to water and soils. It has been shown that marine organisms can concentrate manganese in their bodies to many times the concentration in water.<sup>(111)</sup> In addition, there are less apparent movements of manganese under natural conditions among the components of the ecosystem. The existence of both passive (nonmetabolic) and metabolically dependent pathways of manganese uptake have been recognized.<sup>(116)</sup> In the presence of excess manganese, uptake continues with a consequent build-up in various vegetative parts of the plant. Most plants can tolerate internal manganese concentrations up to 200 ppm without showing adverse effects. The availability of manganese to plants from soils can be evaluated by determining the amount of secondary manganese released from various soil extractants. The secondary forms, in general, are amorphous and represent the bulk of the active manganese fraction in soil.

Many factors will affect the availability of manganese in soil and subsequent uptake by plants; these include concentrations of other cations and total salts, pH, cation exchange capacity, drainage, organic matter content, temperature, compaction, and microbial activity.<sup>(115,117,118)</sup>

Plants apparently absorb manganese primarily in the divalent state. Lowering the soil pH or reducing soil aeration by flooding or compaction favor the reduction of manganese to this form and thereby increases its solubility and availability to plants. The addition of organic matter to soils generally reduces the availability of manganese for plant uptake. A reduction in the population of manganese-oxidizing organisms may increase manganese solubility.<sup>(116)</sup>

Of the trace elements found in the environment, manganese is among the least toxic to mammals and birds.<sup>(119)</sup> Manganese is an essential mineral for nearly all organisms. Most animals can tolerate concentrations of manganese ranging from 500 to 4,920 ppm without evidence of ill effects. Large fluctuations in dietary intake do not result in appreciable changes in the tissue concentrations. Manganese was absorbed in experimental animals following the inhalation of automobile exhaust, as indicated by increased tissue concentrations.<sup>(119)</sup> Higher concentrations of manganese are usually associated with the pigmented portions of the body, pituitary gland, pancreas, liver, kidney, and bones.

The data presented in Table 4-6 seem to indicate that manganese is ecologically magnified in macrophytes and fish in the aquatic environment. This magnification is due to a direct uptake from the water rather than to transport within the food web.

4.3.3.7 Mercury. Mercury is a relatively rare element and there are comparatively few places in the world where it occurs naturally in more than trace amounts. Essentially, the range of mercury in waters in the U.S. is from 0.5 ppb to 10 ppb with the great majority of waters having concentrations of less than 1 ppb. The natural background levels of total mercury in surface and groundwaters is well below 0.5 ppb. The largest use of mercury is in the production of electrical apparatus and in the electrolytic preparation of chlorine and caustic soda. Organic-mercury fungicides have had enormous economic importance since the 1940's in the prevention of seed borne diseases of cereals and flax. Besides the direct use of mercury by man, other activities such as the burning of fossil fuels and land alterations causing erosion increase the cycling of mercury in the environment.

TABLE 4-6. VALUES FOR MANGANESE UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Producers</u>				
Sweet clover	Mn in fly ash**	13.80	Field	62
<u>Terrestrial Omnivores</u>				
Lab rat	<sup>54</sup> Mn orally administered**	4.0	Initially absorbed	120
<u>Aquatic Producers</u>				
Macrophytes	Mn in water**	$1.5 \times 10^{5+}$ (wet weight) $1.4 \times 10^{5-}$	Field	29
<u>Aquatic Carnivores</u>				
Whitefish	Mn in water **	$1.0 \times 10^3$ (wet weight) $1.0 \times 10^5$ (wet weight)	Field, muscle concentration Field, bone concentration	29

\* On a concentration basis.

\*\* Chemical form not specified.

The toxic effects of mercury on aquatic and terrestrial organisms, including man, have been recognized for centuries. In recent years, high mercury concentrations in the food supply of man, causing neurological disorders, e.g., the Minamata disease in Japan, have been discovered. This awareness of the potentially harmful effects has led to a need for an understanding of mercury's behavior in the environment, in both aquatic and terrestrial subsystems. This need has been partially fulfilled, primarily by studies dealing with mercury in the aquatic system. However, the dynamics of the movement of different forms of mercury in aquatic or terrestrial food webs and the relative contributions of the direct uptake component and the trophic component to mercury body burdens in organisms are largely unknown.

Most of the mercury reaching surface waters is deposited in the sediments and subsequently remobilized slowly by microbial and chemical processes<sup>(121,122)</sup> (see Figure 4-7). The concentration of mercury increases from the shallow, near-shore, coarse sediments to the central, deep-water-basin sediments of fine silty clays. This is because smaller particles have a greater surface-area-to-volume ratio and a greater adsorption affinity for mercury.<sup>(123)</sup> The biological cycle of mercury from sediments to waters by benthic organisms and by rooted aquatic plants has been investigated.<sup>(122)</sup> According to Wood<sup>(124)</sup>, the interconversions of mercury compounds are manifested by a dynamic system of reversible reactions, leading to a steady state concentration of methyl mercury in sediments. These interconversions can be catabolized by microorganisms. Although mercury is released into the environment in several organo-mercury compounds or inorganic forms, conversion to the methyl form frequently occurs as a result of bacterial action.<sup>(125)</sup>

Ecological magnification of mercury was noted in soil fungi (Aspergillus niger and Penicillium notatum), in aquatic plants (Elodea densa and Myriophyllum spicatum L.), and in organisms (Gambusia affinis and Carassius auratus) (see Table 4-7). Hardcastle and Mavichakana<sup>(126)</sup> demonstrated fungal uptake of mercury as an important aspect of food chain contamination. Mercury uptake by the fungi varied according to the specific mercury compound present and the mercury concentration in the nutrient cultures. A greater uptake of mercury in the fungi was shown for inorganics

TABLE 4-7. VALUES FOR MERCURY UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Abiotic Components</u>				
Soil-litter	$^{203}\text{Hg}$ -tagged fly ash **	46.3	Microcosm, 139 days	24
Sediment	$^{203}\text{Hg}$ -tagged fly ash **	99.6	Microcosm, 139 days	24
Sediment		97.0		127
<u>Terrestrial Producers</u>				
Moss	$^{203}\text{Hg}$ -tagged fly ash **	0.075	Microcosm, 139 days	24
Grass	$^{203}\text{Hg}$ -tagged fly ash **	0.11	Microcosm, 139 days	24
Forbes	$^{203}\text{Hg}$ -tagged fly ash **	0.09	Microcosm, 139 days	24
Soil fungi (Aspergillus niger and Penicillium notatum)	$^{203}\text{HgCl}_2$ and $\text{CH}_3^{203}\text{HgCl}$ in nutrient culture	$1.09 \times 10^4 \pm 0.49 \times 10^4$	Laboratory	126
Forbes, grasses, and goldenrod	$^{203}\text{Hg}(\text{NO}_3)_2$ in simulated rain	$0.64 \pm 0.50$ $2.73 \pm 2.08$	Field application, 165 days on clipped plots Field application, 165 days on unclipped plots	31
Sweet clover	Hg in fly ash**	8.64	Field	62
<u>Aquatic Producers</u>				
Rooted plant (Elodea densa)	$\text{CH}_3^{203}\text{HgCl}$ and $^{203}\text{HgCl}_2$ solution	$5.19 \times 10^6 \pm 3.35 \times 10^6$	Laboratory	127
Water milfoil (Myriophyllum specatum specatum L.)	Organic and inorganic Hg in solution	$2.21 \times 10^4 \pm 1.76 \times 10^4$	Laboratory, 8 days	122

\* On a concentration basis.

\*\* Chemical form not specified.

TABLE 4-7. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Aquatic Omnivores</u>				
Goldfish ( <i>Carassius auratus</i> )	HgCl <sub>2</sub> in solution	$1.14 \times 10^4 \pm 1.03 \times 10^4$	Laboratory, 81 hours	128
Snail	<sup>203</sup> Hg-tagged fly ash**	0.13	Microcosm, 139 days	24
<u>Aquatic Carnivores</u>				
Fish ( <i>Gambusia affinis</i> )	<sup>203</sup> Hg-tagged fly ash**	0.02	Microcosm, 139 days	24
Fish ( <i>Gambusia affinis</i> )	Hg <sup>0</sup> and HgCl <sub>2</sub> in solution	$2.1 \times 10^4$	Laboratory, 24 hours	129

\* On a concentration basis.

\*\* Chemical form not specified.

than organics; however, organics display greater toxicity. The percent uptake of mercury is greater at lower environmental concentrations; therefore, some organisms can accumulate significant amounts even on exposure to very low trace concentrations.<sup>(128)</sup> Mosses do not assimilate minerals and water from soil but rather derive most of their constituents, including heavy metals, from the atmosphere<sup>(130)</sup>. Mercury ions dissolved in run-off water will accumulate in Dicranum scoparium (a mat-forming moss) if the water contacts any part of the plant.<sup>(131)</sup> Mercury bound in the soil was not available for uptake by the moss, but soil mercury was evidently mobile and leachable by groundwater. Mercury accumulation in vegetable crops is notably in the root portions. The mercury concentration in leaf lettuce, spinach, broccoli, cauliflower, peas, oats, radishes, and carrots was higher in the root portions than the above-ground portion.<sup>(96)</sup> The remaining terrestrial producers, for the most part, exhibit low percent uptake values.

Mercury uptake directly from the water medium is evidenced by percent uptake values of  $5.2 \times 10^6$  for rooted aquatic plants,  $2.21 \times 10^4$  for water-milfoil,  $1.14 \times 10^4$  for goldfish, and  $2.1 \times 10^4$  for fish. Of the mercury in Swedish pike, 50 percent was shown to come directly from the water rather than from the food chain.<sup>(132)</sup> Mercury was found to concentrate initially in the external mucus secreted by fish.<sup>(128)</sup> Additional factors influencing mercury uptake in fish include water hardness, temperature, pH, volume and associated heavy metal ions. Mercury levels in predacious fish (smallmouth bass, rock bass, green sunfish, and yellow bullhead) were shown to be two to three times greater than mercury levels in non-predacious fish (white suckers, carp, common shiners, and chubs).<sup>(123)</sup> The predators appear to accumulate higher concentrations of mercury from their diet because of their position in the food chain; however, predators have higher rates of respiration so greater mercury accumulation may occur due to higher gill irrigation during respiration.

Fish accumulate mercury in aquatic environments, while fish-eating birds may play a major role in transmitting mercury into the terrestrial food chain. Mercury levels in two fish eaters, great blue heron and common tern, far exceeded mercury levels in other species.<sup>(133)</sup> Very high mercury concentrations, up to 17.4 ppm in the liver, were found in fish-eating



birds<sup>(125)</sup>. Osprey feed almost entirely on fish (~ 99 percent of diet), and mercury concentrations in their body tissues appear to be three to five times those of the fish on which they prey.<sup>(121)</sup> In addition, increased levels of mercury concentrations in animals of the terrestrial food chain have been recognized with seed-eating species ingesting methyl mercury-contaminated seed.<sup>(83)</sup>

Mercury concentrations appearing in the body accumulate to the greatest degree in the liver and kidney.<sup>(133)</sup> Mercury retention from inhalation ranges from 10 to 100 percent, depending on the chemical form, aerosol particle diameter, and density.<sup>(83)</sup> Daily consumption of fish containing 5 to 6 ppm mercury may be lethal to humans.<sup>(134)</sup>

In summary, there is evidence of ecological magnification of mercury through the food web in both the aquatic and terrestrial food chain. However, to speak of aquatic food web accumulation without quantification of mercury uptake directly from the water may not be realistic. Aquatic organisms accumulate mercury directly from the water medium and because of their position in the food web, such as is the case with osprey and other fish eating species. There is a need for detailed study on this subject.

4.3.3.8 Selenium. Selenium is erratically dispersed in geologic materials but is usually associated with sulfur and sulfur compounds in sandstone, limestone, and other sedimentary rocks. Average concentrations of selenium in the earth's crust range from 0.03 to 0.8 ppm. The selenium content of black shales and coal is 10 to 20 times the concentration in the earth's crust. The selenium concentration in soils varies with the selenium content of the parent material. Selenium concentration in river water in the United States is normally less than 0.5 ppb<sup>(135)</sup>.

Interest in selenium in the environment and in human diets has increased in recent years. Selenium has been shown to be an essential element when present in trace concentrations but to be a toxicant when present in greater quantities.<sup>(136)</sup> The occurrence of selenium at toxic concentrations in a number of species results from the movement of selenium from highly seleniferous soils through plants to animals. At the other end of the physiological scale, selenium is necessary for the prevention of various degenerative processes, including white muscle disease in

ruminants. Another reason for increasing interest in selenium stems from high selenium concentrations discovered in coal fly ash. It is possible that coal mining and combustion constitute the major movement of selenium in North America<sup>(137)</sup>. However, the selenium in fly ash has been found to be present as elemental selenium, a form which is ordinarily only slightly available to plants or to animals from ingested food.

Selenium is relatively mobile in the terrestrial environment in comparison with the other contaminants of this study. Two references cited in Table 4-8 report 68 and 76 percent of applied selenium retention in the soil. However, as much as 99 percent of the selenium introduced into the aquatic environment accumulates in the sediments. The secondary sources of selenium are biological sinks in which selenium has accumulated. The presence of above-average amounts of selenium in soils does not always affect the uptake of selenium by all plants or, consequently, its presence in the diet of animals. However, selenium accumulator plants (plants that concentrate high levels of selenium) can contain selenium concentrations that are toxic to animals. Plants are usually more tolerant to excessive levels of selenium than are animals. The availability of selenium to plants from soil is determined by various factors; these include the chemical form of selenium in the soil, content of organics and clay in the soil, soil pH, and interactions with other compounds such as phosphates and sulfates in the soil. In general, plants may contain from 0 to 10 ppm selenium; however, concentrations in accumulator plants may range from 50 to 100 ppm. According to Gissel-Nielson and Bisbjerg<sup>(138)</sup>, elemental selenium is generally not available for plant uptake. In addition, selenate forms are much more soluble in soils and more available to plants than selenite forms, and the danger of producing plants containing toxic levels of selenium is much greater with selenates than with selenites. Thus, there is not necessarily a direct relation between the total selenium concentration in the soil and its concentration in plants.

Animals retain 25 to 70 percent of the dietary selenium consumed<sup>(135)</sup>. Factors influencing retention include body stores of selenium as well as the chemical form of selenium present in the diet. In reference to selenium requirements and toxicity, it appears desirable to maintain the

TABLE 4-8. VALUES FOR SELENIUM UPTAKE

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Abiotic Components</u>				
Soil	Sodium selenate solution	68.0	Field, top 9 inches	139
Soil	$^{75}\text{SeO}_2$	75.6	Microcosm, applied as simulated rainfall, 56 days	24
Water	$^{75}\text{SeO}_2$	$\sim 0.7$	Microcosm, 56 days	24
Sediment	$^{75}\text{SeO}_2$	99.0	Microcosm, 56 days	24
<u>Terrestrial Producers</u>				
Pasture herbage	Sodium selenite solution	$\sim 1.0$	Field	139
Ryegrass	Se in soil**	$< 2.0$	Field	140
Sweet clover	Se in fly ash**	13.96	Field	62
Clover	$\text{Se}^0$	0.005	Laboratory	138
	Selenites	1.0		
	Selenates	$46.7 \pm 20.3$		
Barley	$\text{Se}^0$	0.02	Laboratory	138
	Selenites	1.0		
	Selenates	$22.3 \pm 9.0$		
Mustard	$\text{Se}^0$	0.07	Laboratory	138
	Selenites	1.1		
	Selenates	$44.3 \pm 18.8$		
Plants	$^{75}\text{SeO}_2$	8.0	Microcosm, applied as simulated rainfall, 56 days	24

\* On a concentration basis.

\*\* Chemical form not specified.

TABLE 4-8. (Continued)

Sample	Source Form	Percent Uptake/Retention*	Remarks	Reference
<u>Terrestrial Herbivores</u>				
Sheep	$^{75}\text{Se}^{**}$	35.0	Wet absorption	141
Sheep	$^{75}\text{Se}$ -selenious acid	~ 49.0	Laboratory, introduced into rumen, 72 hours	142
<u>Terrestrial Omnivores</u>				
Swine	$^{75}\text{Se}^{**}$	85.0	Net absorption	141
Lab rat	Selenite- $^{75}\text{Se}$	> 50.0	Laboratory, in carcass	143
Lab rat	Wheat containing selenium	~ 40.0	Laboratory, 6 weeks	144
<u>Aquatic Omnivores</u>				
Snail ( <i>Goniobasis clavaeformis</i> )	$^{75}\text{SeO}_2$	< 0.1	Microcosm, 56 days	24
<u>Aquatic Carnivores</u>				
Fish ( <i>Gambusia affinis</i> )	$^{75}\text{SeO}_2$	< 0.1	Microcosm, 56 days	24

\* On a concentration basis.

\*\* Chemical form not specified.

selenium concentration in human and animal diets in the range of 0.05 or 0.1 to 3 or 4 ppm.<sup>(137)</sup>

Referring to the data in Table 4-8, selenium does not appear to magnify in any of the ecological components. The greatest absorption of selenium was shown by swine,<sup>(141)</sup> with a net absorption of 85 percent. The maximum uptake in plants was 47 percent by clover.<sup>(138)</sup> The interactions of selenium in soils, plants, and animals are exceedingly complex and difficult to predict; thus, future research dealing with the transport of selenium from soils to plants to animals is needed.

4.3.3.9 Other Pollutants. As noted in the introduction of this section, nitrogen and sulfur were not considered relevant to the objective of this portion of the study. More specifically, sulfate sulfur, sulfur dioxide, nitrate nitrogen, and nitrogen oxides were not included. Both elemental sulfur and nitrogen are considered to be commonly occurring and biologically essential macro-nutrients to all living organisms. Neither element is known to accumulate in any of the biological compartments in concentrations that are toxic or in excess of that which is normally found in the environment. Therefore, the concern involving these compounds is not their potential accumulation or magnification through a food web, but either the problem of direct contact toxicity or the problem of resultant chemical changes effected by these pollutants on the abiotic components. The Copper Basin at Copperhill, Tennessee, is a prime example of the problems of both direct contact toxicity and long-term abiotic chemical changes resulting from extremely high sulfur dioxide emissions on a terrestrial ecosystem.

#### 4.3.4 Discussion

The objective of this preliminary study of ecological transport and distribution was to review and identify the current state-of-the art on the likelihood of environmental transport within a generic ecosystem of certain specific pollutants that might be generated by a coal cleaning facility. In each section, the specific discussions (1) relate to the individual pollutants under consideration and the parameters controlling the transport and the ultimate ecological fate of each pollutant and (2) deal with the

problems encountered and the limitations to be imposed on extrapolation from the data reported.

All of the pollutants considered in this study have been found to be toxic to living systems above certain concentrations<sup>(145)</sup>. However, the concern here was whether or not those levels of reported toxicity are likely to be reached through normal environmental exposure. That is, even if the source release rate for a specific pollutant from a coal cleaning facility were below the U.S. Government regulation levels, would the pollutant ecomagnify to the point where the concentrations reached the toxicity threshold?

The best method currently in use to predict pollutant concentrations through a food web is that of computer simulation. In order to accomplish this goal of modeling total body burdens or specific organ concentrations of a pollutant, one must be able to use data that reflect all possible exposure routes and that identify the major parameters influencing transport via those routes. Figure 4-5 reflects the individual exposure routes that need characterization and measurement. These types of data, if available, would allow for calculation of the rate transfer coefficients and would allow development of a system simulation model.

A significant finding related to this portion of the study was that data enabling the calculation of rate transfer coefficients were not available. Investigators in general either fail to consider or fail to report:

- (1) Chemical form of pollutant used in the experiment or found in the environment
- (2) Measurement of major parameters affecting transport in their experiments
- (3) Data partitioned into specific exposure sources (i.e., food source, inhalation, and adsorption)
- (4) Experiment time duration.

Therefore, an accurate comparison between the percent uptake or distribution as reported here and the currently reported toxicity levels is beyond the state-of-the-art.

The data reported here represent a synthesis of information from many literature sources. These data reflect the best estimation of what the final fate of each pollutant might be in a generic ecosystem. They do not, however, take into account such important factors as (1) pollutant chemical form, (2) species composition of each functional group, (3) age structure within species and its influence on uptake, (4) seasonal variation (i.e., rainfall, growth rates, and soil water freezing), (5) successional stage variation, and (6) topography, to mention a few.

The information presented here was organized to permit the identification of selected Priority 1 pollutant magnification among the functional components of a generic Northern Appalachian-Midwest ecosystem (Figure 4-3). As emphasized in the sections above, a number of factors, both abiotic and biotic, directly affect the uptake of pollutants by plants and animals. The pollutant's biological and physical distribution and behavior will vary from region to region within the generic ecosystem. This variation is due to the differences of these factors. A statement pertaining to the general behavior of a pollutant, as has been made here, can be misleading if one is not aware of the large possible variations. Therefore, limitations on the usage of the data presented should be imposed. The information should be used as a general identification of ecomagnification and not as an accurate quantification of pollutant transfer. However, future research incorporating the necessary data, previously mentioned, for calculation of transfer coefficients would produce a more accurate quantification.

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## 5.0 DEVELOPMENT OF ENVIRONMENTAL GOALS

Traditionally, adverse health and ecological (H/E) impacts have been identified after a technology becomes operational. Then, suitable mitigations are sought and applied. However, "retrofitted" controls are often costly and may be only partially effective in protecting humans and other living organisms. Comprehensive assessment of potential health and ecological effects associated with coal cleaning facilities probably would confirm anticipated problems and aid in identifying previously unknown problems. In short, a systematic identification of actual H/E problems could lead to better retrofits and aid in the design of new coal cleaning facilities.

The U.S. EPA and others recognize the need for comprehensive and careful interpretation of predicted and observed health/ecological effects associated with coal cleaning technology. However, few methodologies are available for systematically synthesizing and applying pertinent data on biological and ecological effects. As part of EPA's Environmental Assessment Programs, quantitative target values (environmental goals) are being developed for many chemicals, nonchemicals (e.g., heat, noise), and nonpollutant factors (e.g., land use). These environmental goals are based on toxicological and other health/ecological effects data.

This section of the report presents material associated with the development of environmental goals. First, the basic problem and working definitions are provided for environmental goals and associated activities. The scope and research plan are discussed. Then, a review of formulae used by the U.S. EPA's Environmental Assessment Programs shows the basic dose/responses and adjustment factors used in estimating permissible concentrations in air, water, and land. The strengths and limitations of 20 formulae are discussed. The limitations are categorized and a few factors are selected for in-depth analysis. The bulk of the report deals with research to restrict these limitations. Removal of the limitations means improved reliability of formulae for developing environmental goals. Finally, the basic points of the research are summarized and future directions are specified.

## 5.1 Introduction

Many species of organisms exist near coal cleaning facilities. Many of the individuals will be exposed to pollutants from the facilities' emission streams. If pollutants are discharged to the atmosphere, toxic materials may be deposited on plants and breathed by animals. Water-borne chemicals can affect aquatic plants, animals, and microorganisms. Soluble pollutants can be leached from land-filled materials and harm soil organisms, be assimilated by crop species, and enter food chains. Previous sections deal with such transfers. Here, the problem is to determine if the material can harm living organisms, including man, once it is transferred to the organisms.

The burden of proof rests with the health and ecological effects data. Since the application of control technology will be based on health/ecological effects data, the expenditure of millions of dollars to design and implement engineering control systems can best be justified on the basis of carcinogenic/toxicological effects data that are as sound, as complete, and as rigorous as possible. If, for example, no harm is predicted for any of the sensitive organisms in the ecosystem surrounding the coal cleaning facility, then judicious monitoring alone may suffice. If harm of varying types and degrees is predicted, then studies of control technology at the point of origin would be the next step. Chemicals toxic to many species which are emitted in large quantities, of course, would need greater control than chemicals which are toxic to only a few species and emitted in lesser quantities.

### 5.1.1 Basic Problem

The basic need is to obtain high-quality health/ecological effects data and to extrapolate this data correctly. Extrapolation is the activity of inferring or extending known data into an unknown area. Conjectural knowledge of the unknown area is developed based on assumed continuity, correspondence, or other parallelism between it and what is known. Extrapolations of biological effects from (1) the laboratory (where most experiments are conducted) to the field (where most problems lie), (2) one species to another, and (3) one chemical to another are as much an art as a science. However,

incentives are increasing for systematically removing the "art" from such extrapolations, and this report presents several improvements in the state-of-the-art procedures for biological extrapolation.

#### 5.1.2 Working Definitions

Environmental objectives are low concentration levels of pollutant(s) below which humans, other organisms, and ecological systems would not be harmed if the pollutant(s) were released into the air, water, and/or land. These environmental objectives should (1) be based on sound extrapolations which, in turn, are well-based on epidemiological, toxicological, and ecological effects data, (2) be developed in a relatively process-independent manner, and (3) provide control engineers with a quantitative goal against which to compare emission inventories, identify problems, and improve the best available control technology.

There are several types of environmental goals. One, called estimated permissible concentrations (EPC), denotes the maximum allowable long-term concentration of a substance in the ambient media away from a coal cleaning or other facility. A second environmental goal is the minimum acute toxicity effluent (MATE), which is the maximum concentration of a substance at the point of emission for which short-term exposure will not adversely affect a particular species of organism exposed for short periods of time, i.e., acute toxicity does not exist.

The Multimedia Environmental Goals (MEG) chart is the principal tool for displaying environmental goals. The chart, developed at the U.S. EPA's Industrial Environmental Research Laboratory (IERL), has been refined by Research Triangle Institute (RTI)<sup>(1)</sup>, with some assistance from Battelle's Columbus Laboratories. The chart consists of two interrelated tables, (1) a control engineering part including columns for best technology and MATE's, and (2) a health/ecological part including columns for standards/criteria and EPC's both for human health and for ecological systems. The chart has rows for the three media--air, water, and land. The MEG chart is considered an indispensable part of the environmental assessment programs at IERL. Any work on environmental goals needs to be applicable eventually to the MEG chart activities.

### 5.1.3 Scope

The development of environmental goals is associated primarily with the "effects" portion of the basic phases of environmental assessment. Briefly, the basic phases are as follows:

- Source - The coal cleaning facility and its emission streams.
- Transport - The physical, biological, and ecological transfer of toxic substances from the source to receptor organisms.
- Effects - The positive and negative responses of organisms exposed to the transported materials.
- Evaluation - The comparison of environmental objectives to chemical concentrations measured in emission inventories.
- Control - The selection, application, and development of needed control devices and practices.

The interrelationships of these phases are depicted in Figure 5-1. The previous section deals with transport. This section concentrates on the use of dose/response and biological effects data. Properly used, dose/response data will allow the evaluation to be sound and straightforward. Thus, the correct control procedures and devices could be applied to reduce the health/ecological hazard.

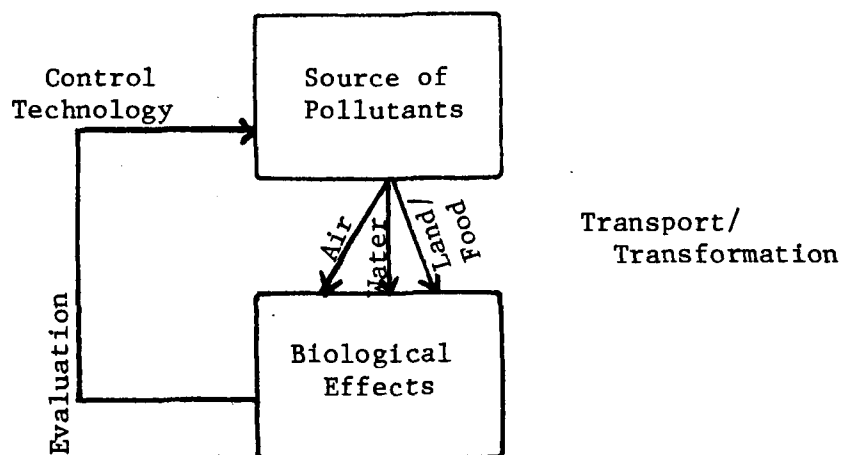


FIGURE 5-1. INTERRELATIONSHIPS OF FIVE PRINCIPAL PHASES OF ENVIRONMENTAL ASSESSMENT

## 5.2 Research Approach

The research approach for this aspect of the study consists of four interrelated steps as follows:

- Clarify scope
- Identify and review formulae
- Evaluate strengths and limitations of formulae
- Restrict limitations.

About two-thirds of the effort was devoted to the removal/reduction of limitations and was regarded as the most critical step.

The research was coordinated closely with other work on development of environmental goals. Scientists at Research Triangle Institute (RTI), North Carolina, are performing the majority of this type of work for IERL. Also, under the U.S. EPA's contract for environmental assessment of fluidized-bed combustion technology, environmental objectives were developed at Battelle's Columbus Laboratories for selected nonchemical and nonpollutant factors; the present coal cleaning work benefited from both projects. Finally, there was dialogue among authors of the other sections of this and other coal cleaning reports. The coordination helped to develop as useful a product as possible.

Over twenty candidate formulae for estimating permissible concentrations were obtained through a search of the literature and evaluated. Formulae identification was assisted by access to RTI's work.<sup>(1)</sup> The literature necessary for the systematic removal of certain limitations was scattered, and the data, when found, had to be adapted. Sometimes the data could not be adapted to the coal cleaning problem. For example, the necessary concepts for optimum use of chronic-effects data could not be developed within the scope of the program and this limited certain activities. And, of course, extrapolation of animal toxicity data to humans looms as one of today's major intellectual challenges.

## 5.3 Review of Formulae

The first major step in the research was to identify and review formulae for estimating environmental goals. These formulae and their



rationales, which are scattered in various reports, ranged in complexity from simple use of raw dose/response data to well-thought-out formulae used in radiological protection. Many notes were assembled about these formulae, their purposes, and rationales; the exercise served to delineate the general state of the art.

As many of the state-of-the-art formulae were being utilized by RTI in their development of environmental objectives for single chemicals, the present research was parallel to part of the RTI work. To facilitate the consistency of the two programs, the identification code used by RTI was adopted by BCL. Additional formulae not used in current MEG chart efforts were also identified; two of these formulae are discussed later as possible approaches for the reduction of limitations of the current procedure.

#### 5.3.1 Basic Formula

The basic form for the equation for calculating environmental goals (EPC's and MATE's) may be simply stated as:

$$\text{EPC or MATE} = \text{dose/response} \times \text{adjustment factor(s)},$$

where dose/response is expressed as an oral LD<sub>50</sub>, TLV (threshold limit value), lowest concentration, or some similar form relating the dose of a particular compound or substance to the response of a particular receptor population. A variety of factors is used to adjust the dose/response data to yield an EPC or MATE. Adjustment factors include exposure time, elimination rates, bio-accumulation, method of exposure, and safety factors. Adjustment factors can be used to correct deficiencies in the dose/response data or to compensate for circumstances peculiar to the unknown situation, such as accumulation of the chemical in tissues that jeopardizes the organism's health.

#### 5.3.2 Overview of State-of-the-Art Formulae

A review of the available formulae for developing EPC's and MATE's for air, water, and land is given in Tables 5-1 to 5-3. All the formulae follow

TABLE 5-1. EPC/MATE FORMULAE FOR THE AIR MEDIUM<sup>(1)</sup>

EPC or MATE <sup>(a)</sup> ( $\mu\text{g}/\text{m}^3$ )	Dose/Response	Basic Equation					Inhalation Factor	Final Form of Equation
		Unit Conversion Factor	Exposure Time Correction	Safety Factor	Correlation Factor	Pollutant Loss Rate		
EPC <sub>AH1</sub>	= TLV ( $\text{mg}/\text{m}^3$ )	$\times 10^3$	$\times 40/168$	$\times 0.01$				= [TLV ( $\text{mg}/\text{m}^3$ ) $\times 10^3$ ] $\div 420$
EPC <sub>AH2</sub>	= Oral LD <sub>50</sub> ( $\text{mg}/\text{kg}$ )	$\times 10^3$	$\times 40/168$		$\times 4.5 \times 10^{-4}$			= LD <sub>50</sub> ( $\text{mg}/\text{kg}$ ) $\times 0.107$
EPC <sub>AH3</sub>	= Oral LD <sub>50</sub> ( $\text{mg}/\text{kg}$ )	$\times 10^3$		$\times 5 \times 10^{-4}$		$\times \frac{0.693}{30}$	$\times \frac{1}{0.143}$	= LD <sub>50</sub> ( $\text{mg}/\text{kg}$ ) $\times 0.081$
EPC <sub>AE</sub>	= Lowest Reported Dose ( $\mu\text{g}/\text{m}^3$ )			$\times 0.1$				= Lowest Reported Dose ( $\mu\text{g}/\text{m}^3$ ) $\times 0.1$
MATE <sub>AH1</sub>	= TLV ( $\text{mg}/\text{m}^3$ )	$\times 10^3$						= TLV ( $\text{mg}/\text{m}^3$ ) $\times 10^3$
MATE <sub>AH2</sub>	= LD <sub>50</sub> ( $\text{mg}/\text{kg}$ )	$\times 10^3$		$\times 100$	$\times 4.5 \times 10^{-4}$			= LD <sub>50</sub> ( $\text{mg}/\text{kg}$ ) $\times 45^{(b)}$
MATE <sub>AH3</sub>	= LC <sub>50</sub> , LC <sub>LO</sub> , or TC <sub>LO</sub> ( $\text{mg}/\text{m}^3$ )	$\times 10^3$		$\times 0.1^{(c)}$				= LC <sub>50</sub> , LC <sub>LO</sub> , TC <sub>LO</sub> ( $\text{mg}/\text{m}^3$ ) $\times 100$

(a) Codes are those used in Reference 1.

EPC = estimated permissible concentration.

MATE = minimum acute toxicity effluent.

A = air; H = health; E = ecology.

1-3 = the number of a particular formula.

(b) The value 45 was developed from adjustment factors and the Monsanto/Handy and Schindler model.<sup>(2)</sup>

(c) Safety factor derived by authors of this report.

TABLE 5-2. EPC/MATE FORMULAE FOR THE WATER MEDIUM<sup>(1)</sup>

EPC or MATE <sup>(a)</sup> ( $\mu\text{g/l}$ )	Dose/Response	Basic Equation							Final Equation ( $\mu\text{g/l}$ )
		Unit Conversion Factor	Air-Water Conversion Factor	TLV to LD <sub>50</sub> Conversion Factor	Safety Factor	Pollutant Loss Rate	Drinking Factor	Concentration Factor	
EPC <sub>WH1</sub>	= EPC <sub>AH</sub> ( $\mu\text{g/m}^3$ )		$\times \frac{30 \text{ m}^3 \text{ air/day}}{2 \text{ l water/day}}$						= EPC <sub>AH</sub> ( $\mu\text{g/m}^3$ ) $\times 15$
EPC <sub>WH2</sub>	= TLV ( $\text{mg/m}^3$ )	$\times 10^3$		$\times 34.5$	$\times 5 \times 10^{-4}$	$\times \frac{0.693}{30}$	$\times \frac{1}{0.029}$		= TLV ( $\text{mg/m}^3$ ) $\times 13.8$
EPC <sub>WE1</sub>	= Lowest TL <sub>m</sub> ( $\text{mg/l}$ )	$\times 10^3$					$\times 0.05$		= TL <sub>m</sub> ( $\text{mg/l}$ ) $\times 50$
EPC <sub>WE2</sub>	= Lowest concentration to cause tainting ( $\mu\text{g/l}$ )								= Lowest concentration causing tainting
EPC <sub>WE3</sub>	= Lowest TL <sub>m</sub> ( $\mu\text{g/l}$ )	$\times 10^3$					$\times \text{ApplicationFactor}^{(b)}$		= TL <sub>m</sub> low ( $\mu\text{g/l}$ ) $\times 10^3$ $\times \text{ApplicationFactor}$
EPC <sub>WE4</sub>	= Maximum allowable concentration ( $\mu\text{g/kg}$ )						$\div \text{ConcentrationFactor}^{(c)}$		= (Maximum allowable Concentration) $\div$ (Concentration Factor) ( $\mu\text{g/kg}$ )
MATE <sub>WH1</sub>	= MATE <sub>AH1</sub> ( $\mu\text{g/m}^3$ )		$\times \frac{30 \text{ m}^3 \text{ air/day}}{2 \text{ l water/day}}$						= MATE <sub>AH</sub> ( $\mu\text{g/m}^3$ ) $\times 15$
MATE <sub>WE1</sub>	= Lowest LC <sub>50</sub> ( $\text{mg/l}$ )	$\times 10^3$					$\times 0.1$		= 100 $\times$ Lowest LC <sub>50</sub> ( $\text{mg/l}$ )

- (a) Codes are those used in Reference 1.  
 EPC = estimated permissible concentration.  
 MATE = minimum acute toxicity effluent.  
 W = water; H = health; E = ecology; A = air.  
 1-4 = the number of a particular formula.

(b) Application factor varies according to recognized criteria.<sup>(1)</sup>

(c) Concentration factor varies for each element. For example, it may be 10,000 for mercury.

TABLE 5-3. EPC/MATE FORMULAE FOR THE LAND MEDIUM<sup>(1)</sup>

EPC or MATE(a) ( $\mu\text{g/g}$ )	Dose/Response	Basic Equation Adjustment Factor			Final Equation ( $\mu\text{g/g}$ )
		Air-Land Conversion Factor	Water-Land Conversion Factor	Crop Uptake Factor	
$\text{EPC}_{\text{LH1}}$	$= \text{EPC}_{\text{WH}} (\mu\text{g/l})$		$\times \frac{2 \text{ l}}{1000 \text{ g}}$		$= 0.002 \times \text{EPC}_{\text{WH}} (\mu\text{g/l})$
$\text{EPC}_{\text{LH2}}$	$= \text{EPC}_{\text{AH}} (\mu\text{g/m}^3)$	$\times \frac{30 \text{ m}^3/\text{day}}{\text{g food/person-day}}$		$\times \frac{\text{yg food}}{\text{zg soil}}$	$= \left( \frac{30 \times \text{EPC}_{\text{AH}}}{\text{g food/person-day}} \right) \times \frac{\text{yg food}}{\text{zg soil}}$
$\text{EPC}_{\text{LE}}$	$= \text{EPC}_{\text{WE}} (\mu\text{g/l})$		$\times \frac{2 \text{ l}}{1000 \text{ g}}$		$= 0.002 \times \text{EPC}_{\text{WE}} (\mu\text{g/l})$
$\text{MATE}_{\text{LH1}}$	$= \text{MATE}_{\text{WH}} (\mu\text{g/l})$		$\times \frac{2 \text{ l}}{1000 \text{ g}}$		$= 0.002 \times \text{MATE}_{\text{WH}} (\mu\text{g/l})$
$\text{MATE}_{\text{LE1}}$	$= \text{MATE}_{\text{WE}} (\mu\text{g/l})$		$\times \frac{2 \text{ l}}{1000 \text{ g}}$		$= 0.002 \times \text{MATE}_{\text{WE}} (\mu\text{g/l})$

- (a) Codes are those used in Reference 1.  
 EPC = estimated permissible concentration.  
 MATE = minimum acute toxicity effluent.  
 L = land; H = health; W = water; A = air; E = ecology.  
 1-2 = the number of a particular formula.

the basic equation described in Section 5.3.1. Differences among them include the type of dose/response data used and the kind and number of adjustment factors employed. More data about each formula are available in RTI's MEG report<sup>(1)</sup> as well as the original source material whose citations are in the MEG report. For example, Handy and Schindler<sup>(2)</sup> developed some of the formulae. Types of dose/response data used are TLV, oral LD<sub>50</sub> for rats, LD<sub>LO</sub>, TL<sub>m</sub>, and lowest concentration to cause tainting. A single type of dose/response information is insufficient; a multiplicity is desirable because

- (1) Dose/response data are associated with particular receptor species (e.g., TLV's are primarily for human exposure; LD<sub>50</sub>'s are for small mammal populations.)
- (2) Lack of data (TLV's may be lacking for the receptor population) requires the use of proxy data.

Generally, the expression best suited to the receptor population and to the needs of the user is employed.

Numerous adjustment factors have been used in the EPC and MATE formulae. These factors modify the dose/response data to fit particular circumstances or needs, often compensating for deficiencies in dose/response information. The factors may be classed into six broad categories--(1) exposure time, (2) exposure pathway, (3) elimination, (4) concentration, (5) safety, and (6) conversion. The exposure time factor is the fraction of the day or week that the receptor population is continuously exposed to the pollution. Exposure is expressed as a concentration, i.e.,  $\mu\text{g}/\text{m}^3$  or ppm. Elimination accounts for the loss of the pollutant from the body through means such as fecal and urinary excretion and is expressed as biological half-life. The concentration factor provides a means to consider accumulation where an organism takes up and concentrates a pollutant, resulting in a body burden greater than might be expected if the chemical were not accumulated. Safety factors are generally included when definitive information concerning safe, tolerable levels of the pollutant are not available and a conservative arbitrary estimate must be made. Finally, conversion factors of three kinds are used. First, a units factor,

generally to convert mg to  $\mu\text{g}$ , is used in most formulae. Second, when only oral  $\text{LD}_{50}$  data are available, an equation is used to convert an oral  $\text{LD}_{50}$  value to a TLV concentration. Third, when dose/response data are not available for the medium of interest, a media conversion factor is applied to convert the EPC from the known medium to the unknown one. It is assumed that the more adjustment factors used, the more accurate the EPC will be. No known formulae use all the adjustment factors described. Some of the more complete formulae include  $\text{EPC}_{\text{AH3}}$  in Table 5-1,  $\text{EPC}_{\text{WH2}}$  in Table 5-2, and  $\text{EPC}_{\text{LH}}$  in Table 5-3. These formulae consider more variables which influence the safe body burden of a pollutant than other formulae and are likely, therefore, to be more accurate.

#### 5.4 Identification of Major Strengths and Weaknesses of Formulae

The strengths and weaknesses of the 20 formulae described in Section 5.3 were evaluated from three viewpoints: media, dose/response data, and adjustment factors. Evaluations were based on common sense and broad professional knowledge of biological systems. Many insights resulted in identifying those limitations most deserving of initial consideration.

In the ensuing discussion, strengths and limitations are discussed from several viewpoints. The evaluation is not meant to be exhaustive, rather it is to provide a reasonable assessment. Finally, all the limitations are listed in one place and they are ranked according to four criteria: relevance, data, time, and expertise. The result of this ranking is the identification of five limitations which are subjected to in-depth analysis in Section 5.5.

##### 5.4.1 Media Viewpoint

From the media point of view, the formulae for breathing (air) are the best. Land formulae are the least defensible or reasonable, with those for water being intermediate. Air formulae have the most quantitative dose/response data of the three media; there are more oral  $\text{LD}_{50}$ 's and  $\text{LC}_{50}$ 's used here than

for water and land formulae. Also, the air formulae tend to have more believable adjustment factors. For example, the exposure-time correction is supported by good reasoning. For ecologically oriented EPC's and MATE's, water formulae probably are the best. This makes sense since fish and other aquatic life forms can be assayed directly and extrapolation from one life form to another is minimal.

Land EPC's and MATE's start with modified dose/response data from air and water predictions. In fact, the EPC's for land are based on EPC's from the other media. Thus, if adjustment factors to basic effects data are not sound for the other media, this distortion would be further reflected in the land EPC's and MATE's. Clearly, the land predictions will require more serious research to make them as rigorous as those for air, for example.

#### 5.4.2 Dose/Response Data

There are also major strengths and weaknesses of dose/response data. Such data are the foundation of all the extrapolation formulae and this subject deserves considerable discussion.

5.4.2.1 Strengths. The formulae use a variety of toxicological measurements rather than only one type of measurement. The TLV (threshold limit value) for air concentration is appropriate to humans in workroom environments and thus does not require species-to-species extrapolation when used for human EPC's and MATE's. Use of the oral LD<sub>50</sub> for rats, the largest known data base for mammals, provided another major data source. The largest data base for toxic effects on aquatic organisms is the LC<sub>50</sub> and this measurement was used in the formulae. Use of LD<sub>50</sub> and LC<sub>50</sub> response data rather than other measurements is a strength because of the ready availability of these two measurements in the published literature.

5.4.2.2 Limitations. On the other hand, the dose/response data included several weaknesses. There are many types of LD<sub>50</sub> measurements, and the non-oral ones were either not used or used without interconverting the non-oral administration route to an oral equivalent<sup>(2)</sup>. The LD<sub>50</sub> is only one of several readily available types of toxicological measurements. For example, the LD<sub>Lo</sub> (lethal dose low or the lowest dose known to kill an individual of a given species) and the TD<sub>Lo</sub> (toxic dose low, i.e., the lowest dose known to be toxic to an organism) are available for many substances when no LD<sub>50</sub> is known. Thus, only a small part of readily available dose/response data is being utilized in the formulae. Likewise, for responses to toxicants by aquatic organisms, there are other types of measurements whose application would strengthen the data base for many of the chemicals; they include such measurements as the LD<sub>Lo</sub> and LC<sub>Lo</sub> (lethal concentration low, i.e., the lowest concentration known to kill an individual of a given species).

There are other limitations. Little attention was given to responses of nonhumans and nonmammals. While humans and similar species may be of paramount importance, protection of other life forms (plants, micro-organisms) is also recognized as being important by the U.S. EPA. Other dose/response data are available but were used sparingly. The toxicological-effects data are for short-term (hours, days or weeks) responses. Long-term (months or years) responses can also be anticipated if a coal cleaning facility continuously emits materials into one of the receiving media. Finally, the dose/response data are for single chemicals, not mixtures of chemicals. Long-term effects and mixtures causing synergisms or antagonisms are more like the "real world" than short-term effects and single chemicals. For example, effects on ecosystem function and mutagenesis are two possible long-term effects that acute bioassays may not indicate. The lack of the above kind of data in formulae is a serious limitation to the accuracy and biological meaningfulness of the EPC's and MATE's.

#### 5.4.3 Adjustment Factors

Adjustment factors also have their strengths and limitations. Unfortunately, these strengths and weaknesses can best be evaluated relative to the degree to which the predictions provide actual or real protection. As this



ideal reference point is not easily attained, again evaluations were based on common sense and professional opinion (derived from a general knowledge of biological systems) instead of experimental data.

5.4.3.1 Strengths. No one adjustment factor seems to extrapolate laboratory-observed dose/response data to the "real world" coal cleaning problem. Rather, a series of adjustment factors have been developed as explained in 5.3.2, each of which can be manipulated individually.

The formulae contain a variety of simple adjustment factors. Indeed, the simplicity of these factors is a strength in that each is usually easy to understand individually. Another strength is the adjustment of one exposure time to another. This is particularly valuable in the air formulae where the TLV (a measurement based on 8 hours of exposure per day for 5 working days per week) was adjusted to 24 hours for the full 7 days or 168 hours of the week. The safety factors, albeit arbitrary, can be viewed as a strength because they are designed to provide a conservative estimate of an EPC or MATE. Development of the research depends on a correlation between the TLV and the  $LD_{50}$ . This correlation<sup>(2)</sup> represents a first step to better utilization of all available dose/response data. For example, if no TLV is known but the  $LD_{50}$  is known, the TLV can be predicted on the basis of the known relationships of TLV's and  $LD_{50}$ 's for other substances. Also, formulae with pollution uptake and loss rate are superior to those without biological half-life data.

5.4.3.2 Limitations. Adjustment factors have major limitations, the greatest of which is the lack of validation about how well they really work. Another major limitation is the lack of certain types of adjustment factors. On the other hand, the ideal EPC's, MATE's, or their equivalent will probably not be forthcoming because of the tremendous expenses in time, money, personnel, and risk to get the ideal information. Rather than despair, the best approach is to identify limitations and attempt to improve the formulae systematically.

Safety factors need a biological basis. Review of background material on safety factors showed that they were often developed arbitrarily. This means that they were created without a biological rationale. For example, safety factors of one hundredth or one tenth of the TLV, LD<sub>50</sub>, or LC<sub>50</sub> have been proposed. Although there is nothing incorrect in establishing an EPC or MATE based on a certain percent of the dose/response data, the safety factor would be more defensible if there were a biological basis for it. The adjustment factors for crop uptake may be limited in their applicability. Some chemicals are not taken up by plants; others are concentrated. More work on an adjustment factor for the food chain transfer is needed.

Omitted factors include extrapolation of data from one species to another. Extrapolation of animal toxicity data to humans for the purpose of creating environmental objectives is an especially controversial area, and is, in fact, very risky. The ecosystem surrounding a coal cleaning facility contains many thousands of species of animals, plants, and micro-organisms. Since laboratory test species are limited to a few tens of species, any formulae for developing environmental objectives would be more powerful if it could allow extrapolation to various species.

Chronic effects, as explained in Section 5.4.2., are a limitation in the dose/response portion of the equation. The lack of an adjustment for chronic effects in the adjustment portion of the equation is also a major limitation.

Other limitations of omission include the lack of

- Adjustment for complex mixtures and consequential synergistic/antagonistic effects
- Adjustment factors for multiple pathways of exposure (the formulae handles breathing, drinking, and eating as if they were independent).

Thus, there are many limitations both of commission and omission.

#### 5.4.4 Selection of Limitations for Analysis

The evaluation of the strengths and weaknesses of the formulae disclosed 16 major limitations deserving investigation. Time constraints allowed the amelioration of only a few limitations. Clearly, a simple method was needed for recognizing which limitations should be studied first, since research to restrict all limitations was not possible at this time.

The identified limitations listed in Table 5-4 were evaluated according to the following 4 (in some cases 5) criteria:

- Relevance     Is the research relevant to the scope of the coal cleaning program?
- Data            Is there sufficient published information available to warrant literature synthesis?
- Time            Is there time within the constraints of the program to start and finish a block of work?
- Expertise      Do Battelle scientists have the expertise to solve the problem?
- Special        For some limitations, the need for research was so great that an additional special category was added.

Although more criteria could have been developed, these five provide a reasonable balance.

The degree of relevance, amount of data, amount of time, and availability of qualified experts were evaluated for each limitation with the use of a 0 to 3 code where 3 means the most relevant, high availability of data, etc. For example, if the limitation was of great relevance it was rated a 3, if of no relevance, the limitation was rated a 0. Intermediate importance was rated 1 or 2. Rankings were based on informed judgement and completed by the senior author in consultation with other authors.

The screening process showed that six of the limitations considered received scores of 10 or greater (10 was an arbitrary cut-off point). The higher the score the less the difficulty in reducing the limitation, and therefore the higher the priority for present research. Topics related to these six

TABLE 5-4. EVALUATION OF POSSIBLE LIMITATIONS IN FORMULAE USED FOR DEVELOPMENT OF ENVIRONMENTAL GOALS

Potential Limitations	Evaluation Criteria					Total
	Relevance	Data	Time	Expertise	Special	
<u>MEDIA FORMULAE</u>						
Air	3	2	3	3		11*
Water	3	2	1	3		9
Land	2	1	1	3		7
<u>DOSE/RESPONSE DATA</u>						
LD <sub>50</sub> not interconverted	3	3	3	3		12*
LD <sub>10</sub> , etc., not used	3	2	2	2		9
Aquatic measurements other than LC <sub>50</sub>	3	2	2	2		9
Plant/microorganism responses	3	2	1	3		9
Chronic data need	3	1	2	3	3	12*
Synergisms/antagonisms	3	2	1	3		9
<u>ADJUSTMENT FACTORS</u>						
Need for validation	3	1	1	3		8
Extrapolation from Species 1 and Species 2	3	2	2	3		10*
Better crop uptake model	3	2	1	3	3	12*
Better safety factors	3	3	2	3		11*
Chronic adjustment	3	1	2	3		9
Synergisms/antagonisms	3	2	1	3		9
Multiple pathways	3	2	1	2		8

\* High priority selections for further research.

1 = little; 2 = intermediate; 3 = most (the higher the score, the less the difficulty of reducing the limitation).

limitations are air formulae that use more available data, LD<sub>50</sub>'s not inter-converted, chronic data, better safety factor, better crop uptake model, and extrapolation from species 1 to species 2.

Five of these limitations are discussed in Section 5.5. The sixth, better crop uptake model, is discussed, in part, in Section 4.0 on ecological/biological transfer.

## 5.5 Research to Reduce Limitations in Formulae

Not all limitations identified in Section 5.4 were considered to be of equal importance. Five limitations were judged to be the highest priority ones to attempt to restrict at this time. The following narrative, tables, figures, and conclusions pertain to these five limitations. They are as follows, in order of their presentation:

- (1) Identification of other formulae - some formulae handle multiple pathways (breathing, drinking, and eating) better than reviewed formulae.
- (2) Correlation of oral LD<sub>50</sub> and non-oral LD<sub>50</sub> routes of administration - the correlation values will increase the accuracy of predictions for certain chemicals.
- (3) Use of chronic effects - more research is needed, but a good foundation was laid.
- (4) Extrapolation of one animal species response to another species - two logical approaches are presented and examples are provided.
- (5) Development of a biological basis for safety factors - the findings have broad implications for formulae for permissible concentrations for air and water.

### 5.5.1 Identification of Other Formulae

Formulae other than those in Tables 5-1 to 5-3 are available. scope of work permitted identification of more than the 20 formulae reviewed

in Section 5.3. When one of the 20 formulae cannot be used to predict an EPC or MATE, then it is possible to use another formula.

Two sample formulae are presented. The two formulae are (1) maximum permissible concentration for radioisotopes, and (2) CUMEX (Cumulative Exposure) Index. No attempt is made to evaluate the two formulae. Rather, a brief explanation is presented here and details are provided in Appendix B. Both are examples of reasonable alternatives to formulae being used in the U.S. EPA MEG activities.

5.5.1.1 Maximum Permissible Concentrations for Radioisotopes. The International Commission on Radiological Protection<sup>(3)</sup> has established maximum permissible concentrations of radioactive materials or radionuclides to which man may be occupationally exposed via inhalation or ingestion. Formulae have been derived for (1) body burden in comparison with radium, (2) body burden based on a permissible RBE (relative biological effectiveness)\* dose rate to the critical body organ, (3) concentrations in air and water (based on an exponential model) taken into critical organs other than the gastrointestinal (GI) tract, and (4) concentrations in air and water based on RBE dose delivered to various segments of the GI tract. The formulae described here are those described for (3) above.

Maximum permissible concentrations are generally based on the RBE dose, burden of the radionuclide in the critical body organ or segment thereof, and the biological half-life of the radionuclide. Depending on the formula utilized in calculating maximum permissible concentrations, the following factors are needed:

- Effective energy - the total energy absorbed in the body organ per disintegration of the radionuclide

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\* Relative biological effectiveness is the ratio of the dose of X-rays or gamma rays, in rads, to the dose of the given radiation, in rads, which has an equal biological effect.

- Standard-man data
- Biological and physical data - average daily ingestion, mass of reference organ, biological half-life, radiological half-life, distribution fractions, concentration in critical organs, etc.

Ideally, the maximum permissible body burden and the maximum permissible concentration of radioactive materials should be based on human studies under working conditions over an extended period of time. However, human data are scarce; therefore, data from animal studies must be extrapolated to man. When animal data are not available, estimates are made from comparison with elements having similar chemical behavior. Because of the many assumptions and approximations made in applying much of the data, detailed refinements in the calculations are deemed to be generally unwarranted. See Appendix B for the equations.

5.5.1.2 CUMEX (Cumulative Exposure) Index. The CUMEX (cumulative exposure) index is a site-specific hazard assessment based on the interrelationships between one or more of the media and biota. The index relates the concentration of the pollutant in the ambient medium to a preselected receptor such as an organ concentration by considering all pathways from the point of measurement to the end point<sup>(4)</sup>.

To apply the CUMEX index, data from the following are necessary:

- Environmental transport models (air, water, land) which estimate pollutant dispersion through air and water, deposition on soil and plant surfaces, uptake by plant, concentrations in air and water, and intake by animals and human exposure through inhalation and ingestion.
- Physiological models which estimate pollutant uptake and subsequent distribution among organs.
- Knowledge of the biological effects of the particular environmental pollutants of concern.

Presently, sufficient data are not usually available for utilizing the CUMEX Index. This index is also limited to single pollutants although multiple pollutants and multiple environmental pathways have been considered. This latter capability makes CUMEX worth considering as a tool to handle multiple pathways. See Appendix B for the equations.

#### 5.5.2 Correlation of Oral LD<sub>50</sub> and Other Routes of Administration

In establishing permissible concentrations of pollutants for continuous exposure, EPA/IERL in cooperation with Research Triangle Institute developed a relationship based upon correlating TLV standards with LD<sub>50</sub> values.<sup>(2)</sup> This work was an extension of the original study in which Monsanto Research Corporation correlated toxicological information for 30 selected agricultural chemicals<sup>(5)</sup>. A regression fit was established for 241 chemicals in the expanded study. The best fit was on the equation for the type where

$$\log (\text{TLV}) = \log a + b \log (\text{LD}_{50})$$

and the value of the constants was found to be

$$a = (0.0125 < 0.0291 < 0.0678) = 95\%$$

$$b = (0.849 < 0.983 < 1.117) = 95\%.$$

By using the lower confidence limit for a safety factor and correcting for fractional work exposure, the following maximum permissible pollutant concentration ( $x_m$ ) was derived\*:

$$x_m \geq 1.07 \times 10^{-4} (\text{LD}_{50}) .$$

The bulk of the toxicity data were oral LD<sub>50</sub>'s for rats; however, if these data were not available, oral LD<sub>50</sub> values for other animals were used (e.g., mouse, guinea pig, dog, cat). If LD<sub>50</sub> data were not reported, oral LD<sub>L0</sub> for rats was used.

Toxicity data for a wide variety of materials via oral administration are not available; however, they are available for other routes (intravenous, subcutaneous, intraperitoneal, inhalation, etc.). Basically, it can be

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\* Maximum permissible concentration ( $x_m$ ) and estimated permissible concentration (EPC) are synonymous here.



assumed that, regardless of the administration route, it should take the same quantity of toxicant in the blood stream to produce a lethal effect, and that each administration route has its own transport efficiency. This will of course, depend upon solubility and chemical reaction within the body for some materials.

The purpose of this study was to try to correlate other routes of administration with the oral route. The procedure followed was to tabulate all rat toxicity data in the Toxic Substances List<sup>(6)</sup> which had information on other routes of administration as well as oral LD<sub>50</sub>. With this information, it was then possible to correlate data using a linear regression analysis. The toxicity data was transformed logarithmically, resulting in the following general equation:

$$\ln (\text{oral LD}_{50}) = a + b \ln (\text{dose/response data for other route of administration}).$$

For the intravenous route, 181 values were used to obtain the following:

$$\ln (\text{oral LD}_{50}) = -.5714 + 1.587 \ln (\text{ivn LD}_{50}).$$

Although there was considerable scatter of the data points, it is not any greater than the Handy and Schindler<sup>(2)</sup> correlation.

To obtain the intraperitoneal/oral correlation, 313 values were used. The linear regression equation is the following:

$$\ln (\text{oral LD}_{50}) = -0.1818 + 1.299 \ln (\text{ipr LD}_{50}) .$$

To obtain the subcutaneous oral correlation, 171 values were used. The linear regression equation is the following:

$$\ln (\text{oral LD}_{50}) = 0.126 + 1.053 \ln (\text{scu LD}_{50}) .$$

Most of the toxicity data utilizing the inhalation route are in the form of LC<sub>LO</sub> (lethal concentration low). LC<sub>LO</sub> is the lowest concentration of a substance in air which has been reported to have caused death in man or to have caused death in animals exposed for 24 hours or less. To obtain the correlation of inhalation LC<sub>LO</sub> and oral LD<sub>50</sub>'s, 101 values were used. Much of the

data were presented in parts per million which then had to be converted to milligrams per cubic meter. The linear regression equation was found to be:

$$\ln (\text{oral LD}_{50}) = -4.64 + 1.389 \ln (\text{ihl LC}_{50}) .$$

This relationship was used to confirm the reasonableness of the following procedure for converting ihl  $\text{LC}_{50}$  to oral  $\text{LD}_{50}$ .

Using a standard 200 g rat with an average breathing volume of 74 cc/min it should be possible to calculate an approximate  $\text{LC}_{50}$  from  $\text{LD}_{50}$  data. Generally, the exposure period for such information is 4 hours, making a total inspiration volume of 74 cc/min x 240 min = 17.76 liters or  $0.0178 \text{ m}^3$ . Recognizing that the weight inhaled is equal to the weight ingested, the relationship can be further developed. For a rat for a 4-hour period,

$$\text{LC}_{50} \times V = \text{LD}_{50} \times W ,$$

where  $\text{LC}_{50}$  is in  $\text{mg}/\text{m}^3$

V is volume inhaled =  $0.0178 \text{ m}^3$

$\text{LD}_{50}$  is in  $\text{mg}/\text{kg}$

W is weight = 0.2 kg .

Therefore,

$$\text{LC}_{50} = \frac{W}{V} \times \text{LD}_{50} = \frac{0.2}{0.0178} \times \text{LD}_{50}$$

$$\text{LC}_{50} = 11.24 \times \text{LD}_{50} .$$

If we assume an  $\text{LD}_{50}$  of 100  $\text{mg}/\text{kg}$ , then the calculated  $\text{LC}_{50} = 11.24 \times 100 = 1,124 \text{ mg}/\text{m}^3$ . The calculated  $\text{LC}_{50}$  using the above linear regression equation is 777  $\text{mg}/\text{m}^3$ . That this value is of the right magnitude, lower than the approximate  $\text{LC}_{50}$ , indicates a reasonable correlation.

Using the above correlations with oral  $\text{LD}_{50}$  values, it should then be possible to approximate an estimated permissible concentration ( $x_m$ ) from rat toxicity data using these other routes of administration.

The above correlations permit non-oral LD<sub>50</sub>'s and LC<sub>50</sub>'s for rats to be converted to an oral LD<sub>50</sub> for rats. The oral LD<sub>50</sub> measurement, in turn, is the dose/response data in some of the equations in Section 5.3. Use of the correlations will improve the quality of dose/response data when no oral LD<sub>50</sub> is available; hence, the quality of the EPC or MATE will also be improved.

Table 5-5 summarizes the equation for performing the conversions.

### 5.5.3 Use of Chronic Effects Data

Dose/response data in the formulae (Section 5.3) are usually for short-term or acute effects. This means that the receptor organisms are exposed to a high dosage of the chemical for a short period of time (hours, days, or weeks). Yet, long-term or chronic exposure (months or years) and effects are more like the real world situation around a coal cleaning facility. In the chronic case, exposure occurs over a long period of time and responses may also occur over long periods of time. For example, the death rate may be altered or the number of malignant tumors in the population may increase. Chronic effects are usually more difficult to quantify than the relatively straightforward LD<sub>50</sub> (lethal dose to 50 percent of the population) and other acute measurements. Thus, chronic effects data are more difficult to compare among themselves than are acute effects data. On the other hand, any progress in the use of chronic effects data is seen as a positive step.

Available published literature was reviewed on the effects of various elements on rodents in (1) life-term, (2) multigeneration, and (3) field/laboratory comparison studies. Attention was given to the 10 priority elements, but other elements also were reviewed. In the experiments, rats and mice lived in environments relatively free of trace contaminants. Dosages of about 5 ppm of specified toxicants were generally given in the drinking water. Standard weighings and autopsies of control and experimental animals showed certain trends.

Most of the data come from the laboratory of H. A. Schroeder<sup>(7-17)</sup>. Information on virus transfer, ethylnitrosourea, and pesticides effects on multigenerations is also available<sup>(18-20)</sup>, but since these materials are not usually associated with emissions from coal cleaning facilities, the articles were used only as auxiliary background information.

TABLE 5-5. EQUATIONS RELATING TOXICOLOGICAL EFFECTS FROM NON-ORAL ADMINISTRATION ROUTES TO THE ORAL ROUTE

Conversions	Sample Size	Equations
ivn LD <sub>50</sub> → orl LD <sub>50</sub>	181	$\ln(\text{orl LD}_{50}) = -0.5714 + 1.587 \ln(\text{ivn LD}_{50})$
ipr LD <sub>50</sub> → orl LD <sub>50</sub>	311	$\ln(\text{orl LD}_{50}) = -0.1818 + 1.299 \ln(\text{ipr LD}_{50})$
scu LD <sub>50</sub> → orl LD <sub>50</sub>	171	$\ln(\text{orl LD}_{50}) = 0.126 + 1.053 \ln(\text{scu LD}_{50})$
ihl LC <sub>50</sub> → orl LD <sub>50</sub>	101	$\ln(\text{orl LD}_{50}) = -4.64 + 1.389 \ln(\text{ihl LC}_{Lo})$ also: $(\text{orl LD}_{50}) = 0.08897 \times (\text{ihl LC}_{50})$

ivn = intravenous

ihl = inhalation

ipr = intraperitoneal

LD<sub>50</sub> = lethal dose fifty

scu = subcutaneous

LC<sub>50</sub> = lethal concentration fifty

orl = oral

LC<sub>Lo</sub> = lethal concentration low

Table 5-6 presents the biological effects associated with an exposure for life-term conditions. Responses of rats and mice did not differ a great deal when data were available for both species. Thus, the following generalizations are believed appropriate to both species. Some elements are virtually innocuous to laboratory rodents; aluminum, barium, beryllium, and tungsten were especially so. Some elements or forms of elements were very toxic to rodents; e.g., selenate, and chromium (VI) were the most harmful. The other 19 were intermediate, with typical responses as follows: increased longevity (chromium III), suppressed weight (indium, scandium, etc.), shortened life span in one or both of the sexes (arsenic, cadmium, etc.), increased number of tumors (palladium, yttrium, etc.). In general, many of the 5-ppm dosages had some adverse effect on the rodents. However, a critical question is whether reproductive capacity was affected.

Chronic effects from the multigeneration or reproductive capacity point of view are shown in Table 5-7. A subset of the elements in Table 5-6 was administered in drinking water to rodents of reproductive age ( $F_1$  = first filial generation) through their progeny ( $F_2$  = second filial generation) to the third filial generation ( $F_3$ )<sup>(12)</sup>. The responses varied. Mice exposed to arsenic survived well, while those exposed to lead died out by the  $F_2$  generation. Rats and mice exposed to cadmium, nickel, selenium, and titanium were intermediate in response compared to the controls. In general, most of the chemicals disrupted reproductive capacity, which would not be evident from acute effects data.

When effects from the life-term and multigeneration studies of the same element and similar dosages are compared, an important generalization emerges. The life-term effects did not indicate the magnitude of the toxicant effect on reproductive status revealed by the multigeneration effects studies. For example, the multigeneration studies showed that cadmium's effects increased in the  $F_2$  generation compared to the  $F_1$  generation. And this trend was also true of effects from nickel, selenium, and titanium. Thus, a relatively minor effect (loss of body weight) in  $F_1$  may not indicate the entire picture of a chronic effect. Effects data from the perspective of many generations are superior to life-term data which, in turn, are superior to data from only one or two weeks of exposure.

TABLE 5-6. SUMMARY OF BIOLOGICAL EFFECTS OF VARIOUS ELEMENTS ON MICE AND RATS DURING LIFE-TERM (CHRONIC) EXPERIMENTS

Element	Symbol	Life-Term Effects on Rats				Life-Term Effects on Mice			
		Dosage (ppm)	Sample Size	Comments	Reference	Dosage (ppm)	Sample Size	Comments	Reference
Aluminum	Al	5	334	Virtually innocuous	(15)				
Antimony (Antimonite)	Sb	5	603	Life span and longevity lessened; nonfasting serum glucose levels lower than fasting; serum cholesterol in soft tissues; not tumorigenic	(11)	5	540	Suppressed growth and longevity in females; not tumorigenic; some accumulation in soft tissues	(10)
Arsenic (Arsenite)	As	—	—			5	643	Shortened life span of oldest 10% males and females; accumulated in organs; not carcinogenic	(9)
Barium	Ba	5	334	Slight growth enhancement; virtually innocuous	(16)				
Beryllium	Be	5	334	Slight growth depression; virtually innocuous	(16)				
Cadmium	Cd	5	461	Arteriolar sclerosis in kidneys; cirrhosis of liver; did not accumulate in kidneys; reduced life span	(8)	5	697	Increased male mortality; longevity decreased in oldest 10% of both sexes; fewer tumors in male than controls	(7)
Chromium (III)	Cr	5	461	Increased longevity in last 10%; females resisted epidemics of pneumonia; did not accumulate	(8)	5	697	No toxicity observed	(7)
Chromium (VI)	Cr	—	—			5	958	Weight suppressed at 8 of 16 intervals; tumors in 28% compared to 27% in controls; all tumors malignant	(13)
Fluorine (Sodium Fluoride)	F	—	—			10	540	Females grew larger than males at older ages; not tumorigenic	(10)
Gallium	Ga	—	—			5	958	Weight suppressed at 14 of 16 intervals; survival of older females less than controls; tumors in 26% relative to 16% in control	(13)
Germanium (Germanate)	Ge	—	—			5	643	Shortened life span of oldest 10% of males; accumulated in spleen with age; not carcinogenic	(9)
Indium	In	—	—			5	958	Weight suppressed at 8 of 16 intervals	(13)
Lead	Pb	5	603	Increased glycosuria; accumulated in soft tissues; coats of males were poor; not tumorigenic	(11)	5	697	Increased mortality in males; longevity less in oldest 10% of both sexes	(7)

TABLE 5-6. (Continued)

Element	Symbol	Life-Term Effects on Rats				Life-Term Effects on Mice			
		Dosage (ppm)	Sample Size	Comments	Reference	Dosage (ppm)	Sample Size	Comments	Reference
Nickel	Ni	5	104	Slight increase in growth; virtually innocuous; did not accumulate in tissues	(15)	5	697	Increased mortality in males	(7)
Niobium (Niobate)	Nb	5	603	Increased glycosuria; not tumorigenic	(11)	5	540	Suppressed growth and longevity in females; increase in hepatic fatty acid degeneration; not tumorigenic; some accumulation in soft tissues	(10)
Palladium	Pd	—	—			5	958	Weight suppressed at 7 of 16 intervals; survival of males greater than controls; tumors in 29% relative to 16% in control; more malignant tumors; appeared to be slight carcinogenic activity	(13)
Rhodium	Rh	—	—			5	958	Weight suppressed at 6 of 16 intervals; tumors in 29% relative to 16% in controls; more malignant tumors; appeared to be slight carcinogenic activity	(13)
Scandium	Sc	—	—			5	958	Weight suppressed at 10 of 16 intervals; tumors in 27% compared to 16% control	(13)
Selenium (Selenate, Selenite)	Se	2, 3	313	Selenite was extremely toxic; selenate did not affect growth but was tumorigenic and carcinogenic in older animals	(14)				
Tellurium (Tellurite)	Te	2	313	Concentrated in kidneys; tellurite did not affect growth, survival and longevity	(14)				
Tin	Sn	—	—			5	643	No toxicity observed; accumulated in spleen with age; not carcinogenic	(9)
Titanium	Ti	—	—			5	697	Longevity decreased in oldest 10% of both sexes; accumulated in organs	(7)
Tungsten	W	5	334	Slight growth enhancement; slight shortening of longevity; virtually innocuous	(16)				
Vanadium (Vanadyl)	V	5	603	Serum cholesterol abnormal; not tumorigenic	(11)	5	643	No toxicity observed; accumulated in organs; not carcinogenic	(9)
Yttrium	Y	—	—			5	958	Growth suppressed at 12 of 16 intervals; tumors in 33% compared to 27% on controls; all tumors malignant	(13)
Zirconium (as metal)	Zr	5	603	Increased glycosuria; not tumorigenic	(11)	5	540	Showed slight toxicity; not tumorigenic	(10)

TABLE 5-7. SUMMARY OF BIOLOGICAL EFFECTS OF SIX ELEMENTS  
ON MULTIGENERATIONS OF MICE AND RATS(12)

Element	Symbol	Dosage (ppm)	Species	Major Responses by F <sub>3</sub> Generation
Arsenic	As	3	Mice	Survived well through F <sub>3</sub> ; no runts; 8 young deaths; 1 failure to breed; only abnormality was a reduction in litter size
Cadmium	Cd	10	Mice	Toxic to breeding mice by F <sub>2</sub> generation; 5 litters had congenital abnormality of the tail; 13% runts; 2 still-born; 3 or 5 pairs failed to breed in F <sub>2</sub> generation
Lead	Pb	25	Mice	Died out by F <sub>2</sub> generation
		25	Rats	More tolerant to Pb than mice; birth in first litters delayed; 35 deaths in F <sub>2</sub> ; 3 pairs failed to breed; 1 dead litter; 173 rats in F <sub>1</sub> and 22 in F <sub>3</sub>
Nickel	Ni	5	Rats	Litter size decreased with each generation; few males in F <sub>3</sub> ; 121 rats in F <sub>1</sub> and 81 in F <sub>3</sub>
Selenium (Selenate)	Se	3	Mice	Strain began to die out by F <sub>3</sub> generation; 24% runts; 7 pairs failed to breed
Titanium	Ti	5	Rats	103 rats in F <sub>1</sub> and 16 in F <sub>3</sub>
CONTROL		—	Mice, Rats	Deaths and runts rare; bred normally for four generations; 209 mice in F <sub>1</sub> and 230 in F <sub>3</sub> for total of 687; 114 rats in F <sub>1</sub> and 113 in F <sub>3</sub> for total of 348

F<sub>1</sub> = first filial generation; F<sub>2</sub> = second filial generation; F<sub>3</sub> = third filial generation.



In addition to life-term and multigeneration studies, a third avenue, field/laboratory comparisons, was explored. The tissue concentrations of rodents exposed to arsenic, cadmium, lead, and vanadium showed that these elements tended to concentrate at higher levels in target organs than did these elements in the same organs of control animals<sup>(7,9)</sup>. The implication for field monitoring is that rodents could be trapped in the area around a coal cleaning facility. Their organs could be removed and analyzed chemically, allowing a comparison of the concentrations in healthy (control) and sick (or exposed) animals, as in Table 5-8. Then assessment could be made about the relative health of small mammals as indicator organisms of the overall health of the ecosystem. Also, the observed elemental concentrations in the small mammals can be related to concentrations for elements in the pathways discussed in Section 4.0.

The implication of the above research is that data on acute responses alone are insufficient. Acute effects data need to be supplemented by chronic data and/or an adjustment made in the formulae. A series of comparisons of acute and chronic effects data were attempted in order to establish a quantitative relationship between the two types of effects. Unfortunately, no commonality was obvious. This means that, until more research is performed, no adjustment can be advanced.

#### 5.5.4 Extrapolation of Response of One Animal Species to Another

Methods of extrapolating from animals to humans depend heavily upon the expirical relationship  $Y = aW^b$  which describes many biochemical parameters (Y) of an organism as a function of the organism's body weight (W)<sup>(21-23)</sup>. For example, Y can be defined as metabolic rate, oxygen consumption, or a particular toxic response. For any specific definition of Y, a and b are constants, so the same equation fits data for mammals whose body weight, W, ranges over several orders of magnitude (i.e., all the way from mice to elephants). Kleiber<sup>(24)</sup> showed that the relationship  $Y = 70 W^{0.75}$ , where W = weight in kg, described total metabolism, Y, in kcal/day for mammals ranging in size from a rat to a steer. Also, this type of equation fits such data more accurately when W represents body weight rather than body surface area<sup>(25)</sup>, although when Y is a toxic response body area may be useful.

TABLE 5-8. TISSUE CONCENTRATIONS OF FOUR ELEMENTS IN ORGANS OF CONTROLS AND EXPOSED MICE AND RATS<sup>(a)</sup>

Element	Symbol	Dosage (ppm)	Exposure Period (days)	Species	Condition	Tissue Concentrations (µg/g wet weight)						Reference
						Kidney	Liver	Heart	Lung	Spleen	Mean	
Arsenic	As	5	1084	Mice	Exposed	1.31	0.43	1.41	1.35	3.93	—	(9)
					Control	1.30	0.02	<0.02	0.11	5.60	—	
Cadmium	Cd	5	1084	Male	Exposed	2.94	0.63	0.20	0.34	0.66	0.93	(7)
				Mice	Control	0.0	0.0	0.0	0.0	0.0	0.0	
		5	1400	Female	Exposed	2.33	0.34	0.42	0.07	0.25	0.70	(8)
				Rats	Control	—	0.01	0.02	0.04	—	—	
Lead	Pb	5	1400	Male	Exposed	0.13	0.22	0.07	0.11	0.24	0.15	(8)
				Rats	Control	0.05	0.06	0.30	0.11	0.09	0.12	
		5.19 0.19	1084	Male	Exposed	1.25	1.37	1.03	1.17	1.42	1.25	(7)
				Mice	Control	0.51	0.37	0.58	0.33	0.53	0.46	
Vanadium	V	5	1084	Mice	Exposed	5.0	2.02	25.3	9.17	19.86	—	(9)
					Control	—	3.38	5.42	4.80	7.38	—	

(a) Average sample size was approximately 20.

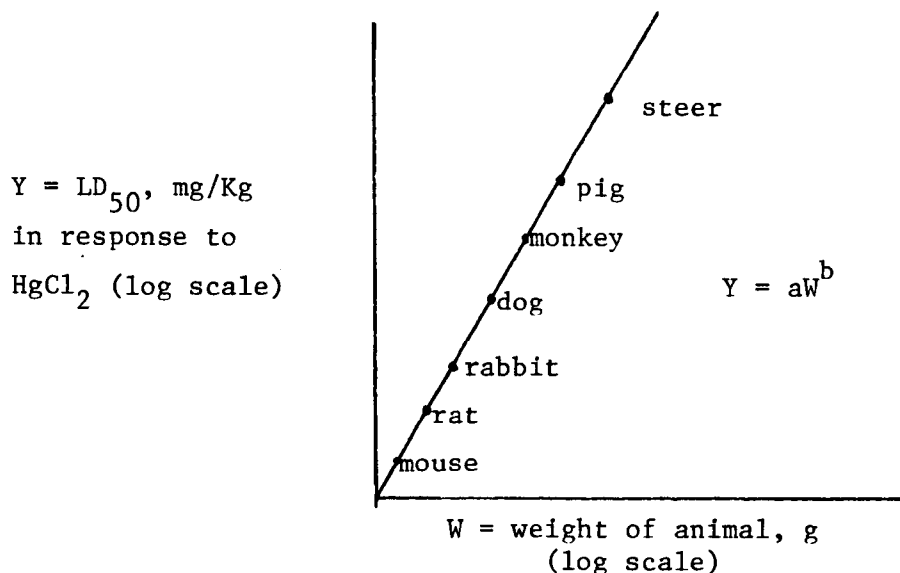
The basic procedure for using the equation  $Y = aW^b$  as a means for extrapolation obviously requires, first, that the equation be explicitly known. That is, W and Y must be clearly defined and quantitatively measurable, and the units in which they are expressed must be specified. Also, the values for a and b must be known (a must be a positive number, whereas b can be either a positive or negative exponent). Once the equation is known, an organism's unknown toxic response (Y) can be predicted from the equation simply by using the organism's known body weight, W, as input to the equation and calculating the predicted Y as output.

The problem which complicates this approach is the fact that the constants a and b usually are not known. Consequently, a and b must be obtained by statistical estimation using a group of (W,Y) data points which have been previously collected. Fortunately, the statistical estimation is quite straightforward because  $Y = aW^b$  converts to a linear function when logarithms are taken of both sides of the equation. That is,  $\log Y = \log a + b \log W$ . Therefore a and b can be obtained by performing a linear regression on log Y data as a function of log W data. Also, the Y,W data should appear to fall approximately on a straight line when plotted on log-log graph paper. Indeed, part of this approach was used in correlating routes of administration (Section 5.5.2).

Two methods for applying basic extrapolation procedures depend on what unknown responses are to be predicted and what kind of data are already available. In Method I the equation deals with only one toxicant at a time, but this single equation can be used to predict the responses of animals of many different species (including man) to that particular toxicant. In Method II, the equation deals with responses to many different toxicants, but it can be used only to extrapolate from the response of one particular species to the response of another species (say, from rat to human). Both of these methods are described in more detail below.

5.5.4.1 Method I. First, one toxicant must be selected for study, and some consistent way of quantifying various species responses to that toxicant must be chosen. For instance, suppose the toxicant is  $\text{HgCl}_2$  and the

form of toxic response to be measured is the  $LD_{50}$ . Then data must be collected from laboratory experiments which determine the  $LD_{50}$ 's for a variety of mammals in response to  $HgCl_2$ . There will be at least one  $LD_{50}$  ( $Y_i$ ) corresponding to each species ( $i$ ) tested. (No exact way exists for determining the minimum number of species which must be tested, but it should include species ranging over several orders of magnitude in size; for instance, mouse, rabbit, dog, and pig.) Then each  $LD_{50}$  ( $Y_i$ ) must be paired with the body weight ( $W_i$ ) of the corresponding animal, and when the resulting set of ( $W_i$ ,  $Y_i$ ) points are plotted on log-log graph paper they should fall approximately on a straight line. The equation of this line is then determined by linear regression as explained earlier. This will yield the values  $a$  and  $b$  in the equation  $Y = aW^b$ .



To interpolate or extrapolate the unknown  $LD_{50}$  for an untested animal, it then becomes a matter of substituting the weight,  $W$ , of that animal into the equation  $Y = aW^b$  and calculating the predicted  $Y$  value. This calculation procedure enables the prediction of the  $LD_{50}$  not only for a human but also for other animals important in a particular ecosystem, such as beaver or deer.

Several illustrative examples of the method of applying Method I may be cited. Figure 5-2 compares the  $LD_{Lo}$  response of three species

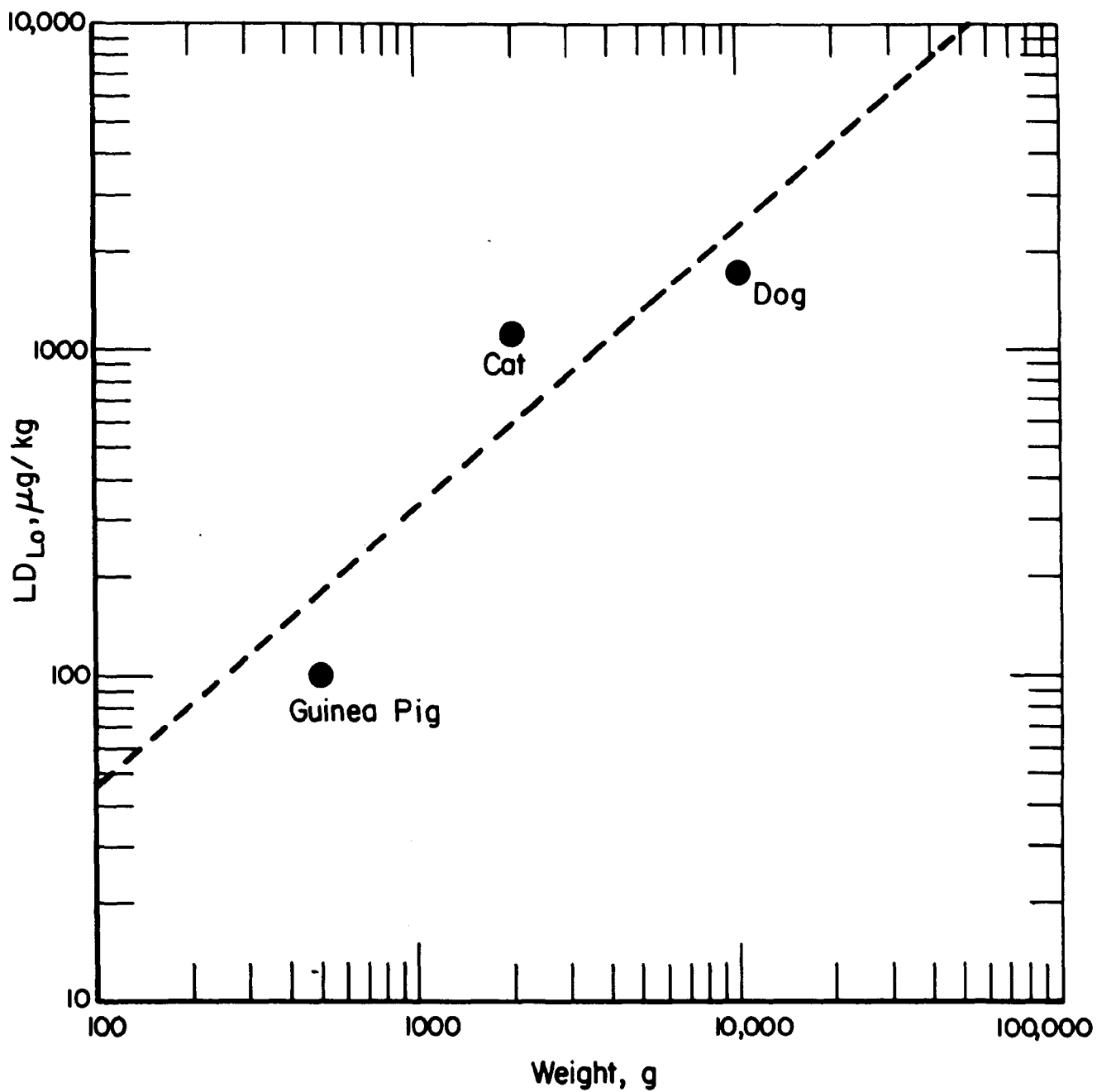


FIGURE 5-2. SUBCUTANEOUS LD<sub>50</sub>'S FOR HYDROGEN CYANIDE

to hydrogen cyanide, administered subcutaneously. The  $LD_{LO}$  values ( $\mu\text{g/kg}$ ) are plotted as a function of the mammals' weights on log-log graph paper. If these weight-response data fit the basic model,  $Y = aW^b$ , the plotted points should appear to fall approximately on a straight line; in this case a rough linear relationship is indicated. The dashed freehand line was drawn to show how the true regression line might look if least squares regression were actually performed on this small set of data.

Figure 5-3 shows another sample application of Method I. Oral  $LD_{50}$ 's in response to arsenic trioxide are plotted as a function of the body weights of three different mammals, including man. In this example, the indicated regression line has a negative slope; this relationship can occur when the exponent, "b", in the equation  $Y = aW^b$  has a negative value. In both Figures 5-2 and 5-3, the hand-drawn dashed lines were included to indicate the approximate positions of actual regression lines which would be used for extrapolation and prediction.

5.5.4.2 Method II. This method uses an equation derived from  $Y = aW^b$  and which can be considered a slight variation of it. Two species of animals must be selected for consideration, the first being one on which laboratory tests can be conducted easily, e.g., a rat, and the second being the one for which extrapolated results are desired (usually, a human). A specific way of quantifying the toxic response must be chosen for each species. For instance, suppose the rat's response and the human's response are to be quantified as the  $LD_{50}$  and the  $LD_{LO}$ , respectively. Suppose further that both responses are to be expressed in term of dose (concentration) per unit weight of body tissue, for instance,  $\text{mg/kg}$ . Then the rat's response ( $X = LD_{50}$ ) to a given toxicant and the human's response ( $Y = LD_{LO}$ ) to the same toxicant will be mathematically related to each other by a fixed constant,  $C^{(26)}$ . That is,  $Y = CX$ . (The body weights of the two animals are indirectly incorporated into this equation through C.)

In order to determine what value C has, data points must be collected whereby the responses of the two species to a variety of toxicants are known.

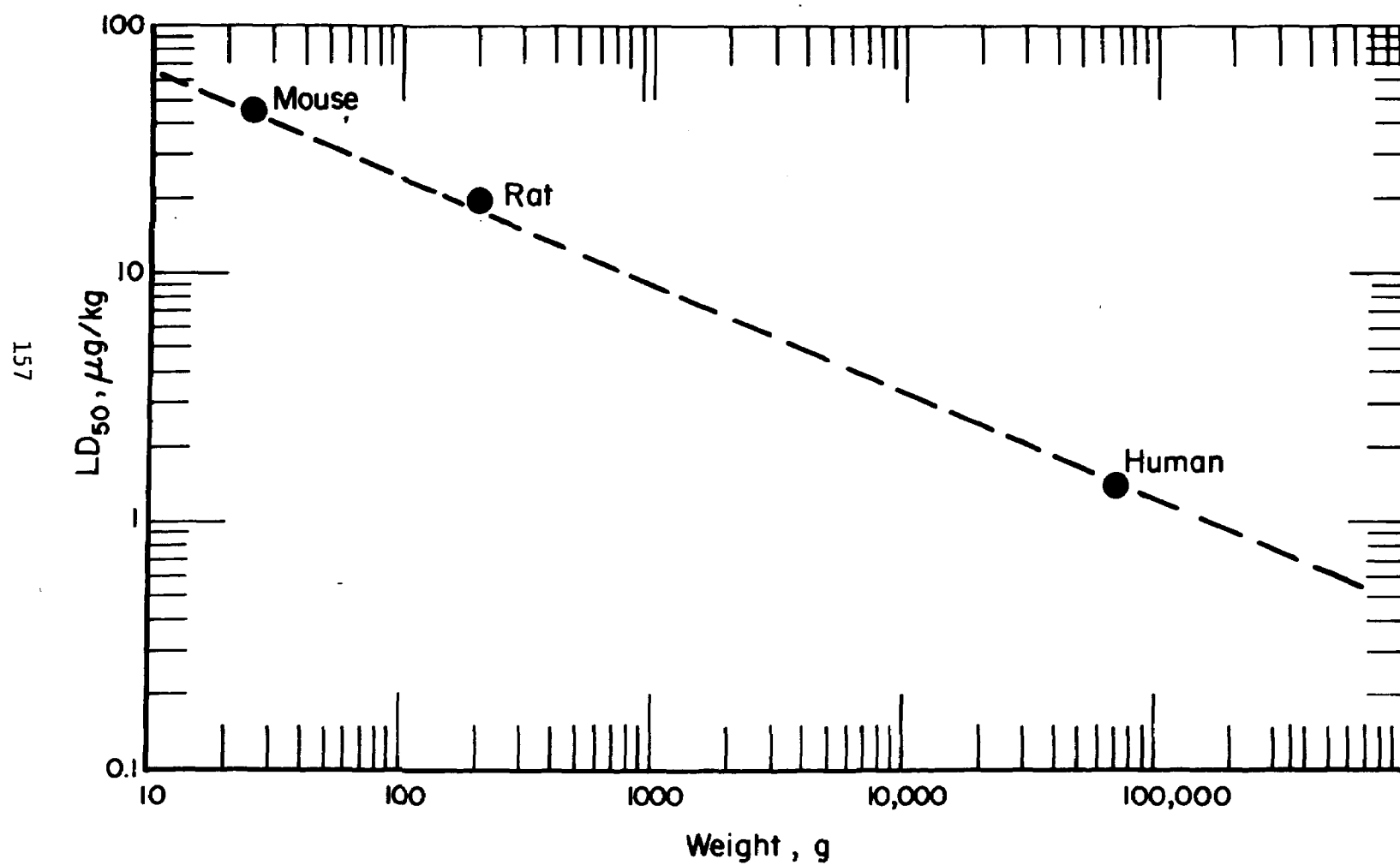
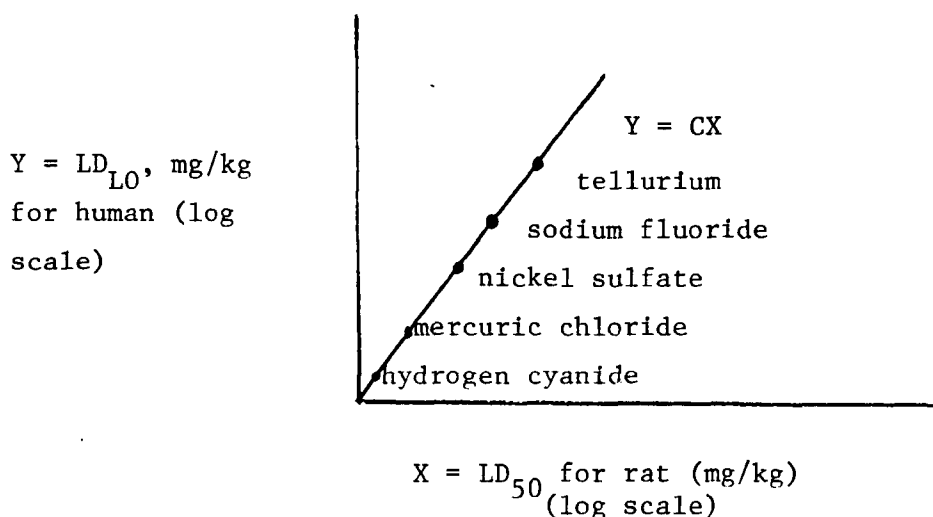


FIGURE 5-3. ORAL LD<sub>50</sub>'S FOR ARSENIC TRIOXIDE

There will then be at least one data point ( $X_1, Y_1$ ) available for each toxicant tested, and the range of responses should cover several orders of magnitude. (The responses of a rat ( $X_1$ ) can easily be obtained from laboratory experiments, although empirical data about the human's response ( $Y_1$ ) may need to be obtained from clinical or industrial exposure observations.) The set of ( $X_1, Y_1$ ) data can then be fitted to a straight line using standard regression techniques and the equation  $Y = CX$  can then be determined.



Finally, this equation can be used to predict the unknown human response to a new toxicant by experimentally determining a rat's response to that toxicant, substituting that  $X$  value into the equation and calculating the estimated  $Y$  value.

Freireich, et al.,<sup>(26)</sup> used this method to derive the equation  $Y = (1/7)X$  describing the relationship between the responses of rats and humans to a variety of cancer drugs.

So far, it has not been possible to provide a good demonstration of either extrapolation method due to the lack of readily available, adequately large sets of parallel data. For many substances, the toxic concentration values reported<sup>(6)</sup> were given using different modes of entry for different test species, and it would not make sense to fit the same equation to data consisting of (for example) oral  $LD_{50}$ 's for rats and subcutaneous  $LD_{50}$ 's for



dogs. The  $LD_{LO}$  is not a very precisely defined measurement; it may be overestimated by one or more orders of magnitude.  $LD_{50}$ 's and  $LC_{50}$ 's are more accurate measurements, but these values comprise a fairly small percentage of the total set of data. In the future, more substantial sets of data will be needed on which to base applications of the models.

5.5.4.3 Comparison of Methods I and II. Each of the methods (I and II) has its own unique advantages and disadvantages. In both methods, it is safer to use the obtained regression line for interpolation than for extrapolation. That is, one will obtain more accurate predictions from the portion of the line falling within the range of the input data points, rather than from the portions of the line extending well beyond this range in either direction.

Method I is more appropriate to use in a situation where only one toxicant is being considered at a time, and the researcher wants to study the effects of that toxicant upon many different species of animals within some ecosystem. Only one equation is needed to estimate all these effects. However, the disadvantages of this method are that a separate equation must be derived for each toxicant, and to fit just one equation requires that the responses of a number of individuals or species of various sizes be known.

Anderson and Weber<sup>(27)</sup> used an equation of the form  $LD_{50} = aW^b$  (Method I) to predict toxic responses of guppies of varying body weights to heavy metal compounds and dieldrin. Krasovskii<sup>(22)</sup> studied the quantitative relationships among the toxic responses of mammals to several hundred chemical compounds and found that the general equation  $Y = aW^b$  could be used to characterize these relationships for 80 to 85 percent of the compounds.

Method II is appropriate to use if man or another species is the only organism whose responses are to be predicted. Only one equation is needed to predict the human responses to a variety of toxicants; and to provide the input necessary to this equation, all that is required is a simple experiment with a laboratory animal. However, the disadvantage of this method is that in order to derive this equation in the first place, prior data on human responses for at least several toxicants is required. Accurate information of this type may not be easy to acquire because direct experimentation involving toxicants in humans is not possible.

#### 5.5.5 Toward a Biological Basis for Safety Factors

Safety factors are often used in formulae that estimate permissible concentrations. The review of formulae showed that safety factors of 10 to 100 were typical. However, the biological rationale for such safety factors usually was not given. The typical approach for developing safety factors has been arbitrariness; thus, there is a need for improved rationales for safety factors. Available data about the ranges of toxicological responses for selected organisms are reviewed in this part of the report. This research is to provide data on which realistic safety factors can be derived empirically.

The scope of the present research permitted identification, assembly, and study of about 15 articles. Pertinent information is presented in two sections, followed by a compilation of selected findings related to safety factors from the two sections. Throughout, responses are presented by type of organisms, e.g., algae, fish, birds. One should recognize, however, that the available data are sketchy. On the other hand, merely getting a qualitative idea of variability of response (and thus the possible threshold of the most sensitive species) to toxicants represents a step forward.

Toxicity levels of compounds in air, water, and soil vary widely. Some substances seem to have no toxic effect at all while others are toxic at concentrations in the parts per billion (ppb) range. Toxic levels and effects of a substance may vary considerably (a) between species, (b) sometimes between subspecies or races, and (c) during different life stages of an organism. For example, toxicity ratios of neonates to adults can vary from 0.002- to 16-fold, a variation of almost four orders of magnitude.<sup>(28)</sup>

Many differences in toxicity can be explained by the quantitative differences in detoxification processes in young versus adult animals. Increased membrane permeability in the young has been suggested as a possible mechanism for age-related differences. Differences in hepatic and clearance ratios that have been shown to occur (possibly involved in age-dependent toxicity effects) may contribute to toxicity variation at both ends of the life span<sup>(28)</sup>.

Variation among species' responses to toxicants is due to many factors such as differences in body size and physiological responses.<sup>(29,30)</sup> As an example, carnivores tend to be more sensitive to toxic materials than herbivores; this is probably due to differences in physiology (e.g., rates of excretion).

#### 5.5.5.1 Ranges of Sensitivity in Selected Aquatic Plants and Animals.

The sensitivity of green algae to cadmium may vary by a factor of 100 between species. Growth is inhibited in Chlamydomonas reinhardtii at concentrations of 0.1 ppm while Euglena gracilis can withstand concentrations up to 10 ppm for seven days with no effects. Some ostracods (zooplankton) have cadmium sensitivity similar to Chlamydomonas.<sup>(29)</sup>

Zooplankton also exhibit interspecific reactions to toxicants. The responses of three species of zooplankton to various metals<sup>(31)</sup> is presented below in Table 5-9. Cyclops is the most resistant, followed by Eudiaptomus, while Daphnia is considerably more sensitive than the other species. The widest range of response is for copper; the ratio of the least sensitive to the most sensitive is 500.

TABLE 5-9. LC<sub>50</sub> CONCENTRATIONS OF VARIOUS METALS FOR  
THREE SPECIES OF FRESHWATER PLANKTON<sup>(31)</sup>

Metal	48-Hour LC <sub>50</sub> , mg/l			Ratio, Least to Most Sensitive
	<u>Cyclops abyssorum</u>	<u>Eudiaptomus padanus</u>	<u>Daphnia hyalina</u>	
Chromium	10.0	10.1	0.022	455
Lead	5.5	4.0	0.60	9
Mercury	2.2	0.85	0.0055	400
Cadmium	3.8	0.55	0.055	76
Copper	2.5	0.50	0.005	500

Frog and toad larvae are sensitive to several metals. Boreal toads (Bufo boreas) will not metamorphose in water whose iron concentration is greater than 30 mg/l. These amphibians are more resistant to acidity than most fish,

but are similar to other anuran larvae and salmonids (fish) in resistance to copper and zinc<sup>(32)</sup>. Leopard frog (Rana pipiens) embryos are much more sensitive to mercury than either larvae or adults by a factor of 100 to 1000, respectively. Sensitivity also varies in the different stages of embryonic development. Ten ppb is lethal to cleavage and blastula stages while the tail bud stage can survive 100 ppb (0.1 ppm) concentration with 90 percent survival. Adults exhibit no mortality in concentrations of 5.0 ppm mercury and less<sup>(33)</sup>. Thus, sensitivity varies by 2 and 3 orders of magnitude.

Salamanders (Ambystoma spp.) and closely related species of different sizes exhibit differential toxicity to beryllium; 96-hour survival in soft water with 10 mg/l beryllium is only 20 percent, while those in hard water exhibit no mortality.<sup>(34)</sup>

Immature fish forms are generally more sensitive than adults; however, this varies with species and toxicants by a factor of at least two. The LD<sub>50</sub> for rainbow trout embryos continuously treated with methyl mercury is approximately 5 ppb, the values for channel catfish and largemouth bass are about 25 ppb, and for goldfish, the LD<sub>50</sub> is 500 ppb.<sup>(35)</sup> The lethal values of mercurial compounds are 580-1300 ppb and 2000-9200 ppb for adult catfish and trout, respectively.<sup>(33)</sup> Fish with large eggs and/or long development time appear to be more susceptible to mercury and perhaps other metals. Fish embryos, larvae, and early juveniles (ELEJ) are more sensitive to cadmium than are adults. ELEJ sensitivity to mercury, lead, and zinc often varies with species.<sup>(36)</sup> Relative interspecific sensitivity of some fish species to various metals is presented in Table 5-10.

TABLE 5-10. SENSITIVITY OF EARLY JUVENILE FISH TO VARIOUS METALS<sup>(36)</sup>

Metal	Sensitivity Range	
	Most	Least
Cadmium	Brooktrout > Flagfish > Bluegill > Fathead Minnow	
Copper	Brooktrout > Fathead Minnow > Bluegill	
Chromium	Brooktrout > Fathead Minnow	
Lead	Flagfish > Brooktrout	
Mercury	Fathead Minnow > Flagfish > Brooktrout	

#### 5.5.5.2 Ranges of Sensitivity to Toxicants of Selected Terrestrial

Animals. Embryos of birds tend to be more susceptible to metals than adult forms. Chicks are very sensitive to selenium poisoning. In fact, areas with high levels of naturally occurring selenium are first detected by low hatchability of chicken eggs; the eggs exhibit no sign of poisoning and may be fertile, but they do not hatch because of malformed or deformed embryos.<sup>(37)</sup>

The  $TL_{50}$  of selenium and other metals for chick embryos is as follows: selenium and arsenic together - 0.01 ppm; arsenic alone - 0.05 ppm; methyl mercury alone - 0.1 ppm; mercury and lead together - 1.0 ppm.<sup>(35)</sup> Adult mallards are generally more resistant to toxicants than are bobwhites and pheasants, except for terpene polychlorinated and some mercury compounds. Pheasants are about three times as resistant to Ceresan M in feed as mallards ( $LC_{50}$  of 146 and 50 for pheasant and mallard, respectively).<sup>(38)</sup>

Fetal and newborn mammals tend to be more susceptible to some metals (e.g., selenium, mercury, arsenic, iron) than adults, and females are more sensitive to selenium than males.<sup>(39-41)</sup> Selenium in the diet in excess of 5 ppm may cause chronic toxicity; 10 ppm fed to sows results in pigs that are small, weak, or dead at birth. Malformed or deformed young may occur in pigs, sheep, cattle, and rats on a seleniferous diet.<sup>(37)</sup> Selenium is an essential micronutrient, but if it occurs in excess it may interfere with reproduction, even at subtoxic levels.<sup>(41)</sup> The range of adult to newborn toxicity ratios for many pharmaceutical compounds was about 0.1 to 50 and averaged around 4.5 for a subset of 62 nonpharmaceutical chemicals on the list of 400.<sup>(39)</sup> Perhaps a rule of thumb, then, is that baby mammals are four or five times as susceptible as their adult counterparts.

#### 5.5.5.3 Selected Findings Related to Safety Factors.

The following selected findings bring together in one place the more quantitative relationships discussed in the previous two sections on safety factors.

- (1) Differences in toxicity of a substance to different species or ages is due in part to physiological and metabolic differences and body size.

- (2) Herbivores are generally more resistant than carnivores.
- (3) The green algae Chlamydomonas reinhardi is 100 times more sensitive to cadmium than the algae Euglena gracilis.
- (4) The zooplankton Cyclops abyssorum is 455 times, 9 times, 400 times, 76 times, and 500 times more resistant to chromium, lead, mercury, cadmium, and copper, respectively, than Daphia hyalina. Eudiaptomus padanus is intermediate in sensitivity.
- (5) Boreal toads will not metamorphose in iron concentrations greater than 30 mg/l.
- (6) Leopard frog embryos are 100 times and 1000 times more sensitive to mercury than larvae and adults, respectively. The cleavage and blastula stages are the most sensitive stages in embryonic development.
- (7) Beryllium is not differentially toxic to salamanders of various ages, but is at least 5 times as toxic in soft water as in hard water.
- (8) Rainbow trout and channel catfish larvae, respectively, are 116 to 260 times and 80 to 360 times more sensitive to mercury than the adults. Fish species with large eggs and/or long development times are the more sensitive species.
- (9) Bird embryos are more sensitive than adults and are especially sensitive to selenium.
- (10) Mammalian fetuses are more sensitive than adults. New born are about 4.5 times as sensitive to arsanilic acid, 1.5 times as sensitive to ferrous sulfate and lead arsenate, and 0.6 to 0.9 times as sensitive to some mercury compounds as adults.
- (11) Few studies exist that compare sensitivity to metals in developing young and adult homeotherms.

## 5.6 Application of Improved Formulae

Application of the findings is the next most important step. Some of the advances in the state of the art can be implemented immediately, while others still require more "fitting" of the solution to the problem. For example, the interconversion of various types of  $LD_{50}$ 's can be utilized any time there is no oral but there are non-oral  $LD_{50}$  measurements. The additional formulae certainly can be used in future refinements of estimating environmental goals in air and water.

Extrapolation of dose/response data from one species to another is not as straightforward as one would like. On the other hand, some generalizations can be applied. Generally, the larger the weight and surface area of an organism, the greater the relative dosage needed to adversely affect that species. Using this and other concepts, predictions of how another species would respond in general can be made.

More conceptual work is needed on understanding chronic effects before these data or adjustments to formulae using acute effects can be attempted.

Safety factors, which are a function of the test species, now have a much stronger data base. A safety factor of 1000 is appropriate for aquatic populations when the available dose/response data are from one of the less sensitive species in the ecosystem. Thus, the insensitive as well as the sensitive species can receive protection. If, on the other hand, available dose/response data are for sensitive aquatic species, then a much smaller safety factor would be needed for protecting all less sensitive species in the ecosystem. For terrestrial situations, safety factor recommendations are more difficult to establish. However, a safety factor of at least 10 is justified biologically.

## 5.7 References

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## 6.0 DECISION CRITERIA FOR PRIORITIZING POLLUTANTS, SOURCES, AND PROBLEMS

There are major differences in the hazards posed to man and the environment from different pollutants released as a result of coal cleaning processes. One of the objectives of this study is to establish criteria for rating the relative importance which should be placed upon identifying and controlling specific pollutants from coal cleaning processes.

The position has never been taken during the investigation that pollutants from coal cleaning processes could be prioritized into an ordinal array, from the worst to the least. Rather, it has been considered that this is an unattainable ideal and that a more realistic goal is to categorize them into groups of varying degrees of hazard.

As noted in the Introduction, the fundamental criterion for ranking the importance of any pollutant is the relationship between its expected environmental concentration and the maximum concentration which presents no hazard to man or biota on a continuous long-term basis. The estimated environmental concentrations (EEC) of pollutants can be projected on the basis of coal feedstock, process configuration, control devices applied, environmental dilution and dispersion, etc. In the case of actual coal cleaning processes, the EEC of pollutants can be measured by Level 1, Level 2, or Level 3 analyses.

The other half of the relationship, the estimated permissible concentration (EPC), is quite another matter. As discussed in Section 5.0, the toxicological and epidemiological data needed to characterize the relative health and ecological risks of the pollutants to be expected from coal cleaning processes are woefully inadequate. The information base is in far better shape for many of the chemical compounds encountered in the chemical and similar industries, but almost none of these are of any concern to coal cleaning. Actually, the exact chemical form of many coal cleaning pollutants is unknown more often than not. There appears very little likelihood that the EPC data base for coal cleaning pollutants will improve dramatically in the near future.

Thus, in spite of its undeniable theoretical soundness, the EEC/EPC relationships probably will be unable to provide substantial prioritization guidance over the near term.

Looking toward the longer term, one of the U.S. EPA's contractors, the Research Triangle Institute, is developing the concept of multimedia environmental goals (MEG's), of which health-related and ecology-related estimated permissible concentrations for air, water, and land are key parameters. Current status of this ongoing effort has been described by Cleland and Kingsbury.<sup>(1)</sup> Because of the data insufficiencies mentioned above, the MEG tabulations for pollutants from coal cleaning processes are incomplete, which limits the present application of MEG's.

Another approach to the estimation of acceptable concentrations utilizes Minimum Acute Toxicity Effluents (MATE's). These are considered to represent the very approximate maximum concentrations of pollutants in air, water, or land effluents without adverse effects for short-term exposure. As developed by researchers at Research Triangle Institute<sup>(1)</sup>, six MATE concentrations may be described for a single compound; two MATE's based on health and ecology for each medium. While there are also large gaps in the toxicological data needed to estimate MATE's, the types of data from which MATE's can be derived, e.g., TLV's, LD<sub>50</sub>'s, LD<sub>LO</sub>'s, LC<sub>50</sub>'s, TD<sub>LO</sub>'s, etc., do not require the extrapolations which are necessary to convert them to EPC's (see Section 5.0) and are thus more amenable to empirical treatment.

Source Analysis Models (SAM's) have been developed by Acurex, another of the U.S. EPA's contractors, to assist in comparing elements of an environmental assessment. The simplest SAM, designated SAM/IA, is designed for rapid screening of effluent streams and assumes no effluent transport or transformation. As described by Schalit and Wolfe<sup>(2)</sup>, rapid screening of the degree of hazard and the rate of discharge of toxic pollutants may occur at any level of depth of chemical and physical analysis and may even be used to provide guidance for Level 2 analysis. In SAM/IA, effluent concentrations are compared to the appropriate MATE's; the comparison may also evaluate the difference between an uncontrolled process and one with pollution controls.

SAM/IA also estimates a "degree of hazard" (H) which is the ratio of a specific pollutant concentration in an effluent stream to its corresponding

health-based MATE; the total stream degree of hazard can be calculated by summing the individual H's.

Similarly, Toxic Unit Discharge Rates (TUDR's) can be estimated by multiplying the degree of hazard (H) by the stream flow rate; these too can be summed for the total stream. At present the narrowness of the data base on MATE's also limits the application of SAM/IA to coal cleaning processes.

For the near term, a pragmatic approach to prioritization is possible, based on the assumption that the relative importance of a pollutant can be based generally on its toxicity and its abundance and that those substances for which criteria have been established or which have been designated as pollutants are important. The preliminary "Priority 1" list of pollutants (see Section 3.1) had its origin in these considerations. The relative importance for investigation probably has increased for the 13 inorganic elements and their compounds because of their inclusion in the list of 65 toxic pollutants being considered for effluent limitations, as listed in Table 3-8.

An important modifying parameter influencing the prioritization of a pollutant is the availability, or lack of availability, of adequate pollution controls. A high-risk pollutant, for which state-of-the-art controls are inadequate, should have top priority for the development of adequate controls. More information on adequacy of control, by pollutant, is needed to apply these adjustments to relative rankings.

Preliminary working prioritization lists can be derived by comparing the emission concentrations (uncontrolled and controlled) in each stream (air or water) with the concentrations established by air or water quality criteria or by regulation. These concentration levels may be health- or ecology-based, or both; or they may reflect available technology, e.g., "best available control technology" (BACT). Such lists will provide a working basis for prioritization of R&D efforts while the more precise and sophisticated MATE's and MEG's are being perfected.

## 6.1 References

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## 7.0 RECOMMENDATIONS FOR FUTURE WORK

While this research effort has developed a sound understanding of the types and forms of the environmental assessment criteria needed in support of the coal cleaning environmental assessment program, the perceived problems existing at its commencement have not all been answered, and major new problems have been uncovered along the way.

Thus, the basic recommendation for future work is to continue to bring to completion the tasks already begun. Several more specific recommendations can also be made. The order is not chronological, although the output of one subtask can be the input to another. Also, some of the more complex and fundamental problems will require long-term research for their full elucidation.

### 7.1 Potential Environmental Pollutants

The Priority 1 list of pollutants should be reassessed when better estimates of emissions and EPC's are available, in order to winnow out marginally important pollutants and focus attention and efforts on the truly important ones. Concomitantly, a number of potential pollutants omitted from that list should be reassessed to reconfirm the correctness of the omission.

### 7.2 Estimation of Environmental Concentrations

The physical transport and dispersion models which are to be recommended should be selected and exercised on simulated coal cleaning and utilization systems to demonstrate their appropriateness and applicability. As soon as possible, these models should also be validated in the field using actual data and modified as suggested by field experience.

With respect to ecological transport and fate, the recommendations for future research fall into three major categories. First, there is an immediate need to conduct research designed to determine the relative importance of each exposure pathway for a series of populations within each compartment. A series



of closely controlled experiments could be designed to estimate these values. This would enable concentrated effort to be focused on the second major category, which is the determination of the rate transfer coefficients for each dominant pathway and the controlling parameters for each. The third category of recommended research is simulation model development and field test validation of the forecasts obtained from such models. An orderly timing of these research recommendations could produce an accurate short-term index of anticipated impact from released trace contaminants from a coal cleaning facility.

### 7.3 Development of Environmental Goals

Several recommendations can be suggested in this complex area, which has possibly the most uncertain base for environmental assessment. More work needs to be conducted on methodology which will permit making better use of the variety of toxicological and epidemiological data which are available. For example, data are available on animals other than laboratory rodents and fish, on vegetation, and on microorganisms. Epidemiological data exist that should be taken advantage of. Also, a wider range of toxicological measurements needs to be utilized; this includes  $TD_{LO}$ ,  $LD_{LO}$ , and others. One specific task would be to interconvert the various toxicological measurements from the less frequently used ones to a more standard measurement, i.e.,  $LD_{50}$ .

Adjustment factors in the formulae for estimating permissible concentrations need to be improved simultaneously with the use and development of more and better effects data. A literature review of synergistic/antagonistic effects would help to close one of the larger data gaps. Such a review would be indispensable in interpreting the results of bioassays using complex mixtures. Other adjustment factors need to be included too. For example, more work is warranted on the relationship of chronic versus acute effects and how to adjust acute effects data when an approximation of chronic effects is needed. Special attention should be directed to chronic effects involving irreversible alteration of genetic material.

Present formulae deal with only one pathway at a time. Formulae that handle exposure from multiple pathways should be further identified and/or developed.

The development and refinement of environmental goals should continue. They should be developed for electromagnetic radiation, water usage, and complex mixtures in effluents. The environmental goals for single chemical species should undergo continuous refinement, particularly the systematic reduction and removal of deficiencies in the prediction formulae. All findings need to be incorporated into the MEG concept.

APPENDIX A

SAMPLE COMPUTER PRINTOUT FOR EMISSION  
CONCENTRATION MODEL

# APPENDIX A

## SAMPLE COMPUTER PRINTOUT FOR EMISSION CONCENTRATION MODEL<sup>(a)</sup>

INPUT DATA FOR THIS RUN ARE PRINTED BELOW

ANALYSIS GIVEN IMMEDIATELY BELOW REFERS TO CLEANED COAL PRODUCT  
CARBON= .75800 H2= .05070 O2= .03300 SULFUR= .01660 N2= .01340  
ASH= 0.12700 BTU= 13526.0/LB

ANALYSIS GIVEN BELOW REFERS TO TRACE CONSTITUENTS IN RAW COAL

NAME	FRACTION	NAME	FRACTION	NAME	FRACTION	NAME	FRACTION
PYR S	.1820E-01 <sup>(b)</sup>	ORG S	.4500E-02	SUL S	.5000E-03	N	.1160E-01
AS	.2400E-04	CD	.1000E-06	PB	.1450E-04	HG	.3900E-06
FE	.2180E-01	MN	.4500E-04	BE	.2600E-05	SE	.3000E-05
AL	.2860E-01	ZN	.6200E-04	NI	.1710E-04		

MASS FRACTIONATION FACTORS TO CLEANED COAL AND REFUSE RESPECTIVELY FOR  
THE COAL WASHING STAGES ARE GIVEN BELOW  
0.8000 0.2000

TRACE FRACTIONATION FACTORS FOR COAL CLEANING TO CLEANED COAL ARE GIVEN  
BELOW. FRACTION TO REFUSE IS ONE MINUS FRACTION TO COAL.

NAME	FRACTION	NAME	FRACTION	NAME	FRACTION	NAME	FRACTION
PYR S	.5000	ORG S	.8700	SUL S	.5000	N	.8700
AS	.5300	CD	.5300	PB	.6700	HG	.5300
FE	.5300	MN	.5300	BE	.6700	SE	.5300
AL	.4700	ZN	.6000	NI	.6000		

ASH, BTU, AND SULFUR CONTENTS RESPECTIVELY OF RAW COAL ARE GIVEN BELOW  
0.2367 11689.0 0.0232

PROCESS WATER REQUIREMENT IS GIVEN BELOW IN TONS PER TON OF RAW COAL  
1.770

AIR FLOW FOR THERMAL DRYER IS GIVEN BELOW IN MSCF PER TON OF CLEAN COAL  
FROM DRYER  
26.00

FRACTION OF CLEANED COAL PRODUCT PROCESSED BY THERMAL DRYER IS GIVEN  
BELOW  
1.000

EXCESS AIR FOR COMBUSTION IS GIVEN BELOW AS 1 PLUS FRACTION FOR EXCESS  
AIR  
1.100

(a) See Section 4.1.2, "Estimation of Emission Concentrations", for brief  
discussion of model.

(b) E-01 means  $10^{-1}$ , etc.

TRACE FRACTIONATION FACTORS FOR COMBUSTION PROCESS TO SLAG ASH ARE GIVEN BELOW FOR EACH CONSTITUENT. FRACTION TO AIR IS (1 - FRACTION TO ASH) X (1 - PRECIPITATOR REMOVAL EFFICIENCY)

NAME	FRACTION	NAME	FRACTION	NAME	FRACTION	NAME	FRACTION
PYR S	.0000	ORG S	.0000	SUL S	.0000	N	.0000
AS	.1090	CD	.6710E-01	PB	.4070E-01	HG	.7000E-02
FE	.3110	MN	.2630	BE	.0000	SE	.1040E-02
AL	.2930	ZN	.4030E-01	NI	.1590		

REMOVAL EFFICIENCIES FOR ELECTROSTATIC PRECIPITATOR AND THERMAL DRYER SCRUBBER RESPECTIVELY ARE GIVEN BELOW FOR EACH TRACE ELEMENT

PYR S	0.0000	0.5000
ORG S	0.0000	0.5000
SUL S	0.0000	0.5000
N	0.0000	0.5000
AS	0.9814	0.9800
CD	0.9699	0.9600
PB	0.9636	0.9600
HG	0.1163	0.5000
FE	0.9943	0.9900
MN	0.9931	0.9800
BE	0.9000	0.7500
SE	0.8571	0.7500
AL	0.9957	0.9900
ZN	0.9809	0.9800
NI	1.000	0.9900

EMISSION FACTORS FOR NOX, PARTICLES, HYDROCARBONS, AND CO ARE GIVEN BELOW. ALL BUT PARTICLES ARE LBS PER TON. PARTICLES EMISSION FACTOR IS LB/TON/% ASH.

18.00	16.00	0.3000	1.000
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NUMBER PRINTED BELOW INDICATES ENERGY SOURCE FOR THERMAL DRYER: 0 = RAW COAL; 1 = CLEAN COAL

0

CALCULATED RESULTS FOR THIS RUN ARE PRINTED BELOW

TRACE ELEMENT ANALYSIS FOR CLEANED COAL IS GIVEN BELOW

NAME	FRACTION	NAME	FRACTION	NAME	FRACTION	NAME	FRACTION
PYR S	.1138E-01	ORG S	.4894E-02	SUL S	.3125E-03	N	.1261E-01
AS	.1590E-04	CD	.6625E-07	PB	.1214E-04	HG	.2584E-06
FE	.1444E-01	MN	.2981E-04	BE	.2177E-05	SE	.1988E-05
AL	.1680E-01	ZN	.4650E-04	NI	.1283E-04		

REQUIRED QUANTITIES OF CLEANED COAL AND RAW COAL FOR 1 MILLION BTUS OF ENERGY INPUT TO COMBUSTION ARE GIVEN BELOW

73.93 LB                      93.27 LB

TOTAL AMOUNT OF WASTE WATER STREAM INCLUDING REFUSE AND THE AMOUNT OF REFUSE COMPONENT THAT HAS BEEN ADDED TO THE WATER ARE GIVEN BELOW.

183.7 LB                      18.65 LB

TRACE ELEMENT ANALYSIS OF TOTAL WASTE WATER STREAM IS GIVEN BELOW

PYR S	.4619E-02	ORG S	.2970E-03	SUL S	.1269E-03	N	.7655E-03
AS	.5726E-05	CD	.2386E-07	PB	.2429E-05	HG	.9305E-07
FE	.5201E-02	MN	.1074E-04	BE	.4355E-06	SE	.7157E-06
AL	.7694E-02	ZN	.1259E-04	NI	.3472E-05		

TRACE ELEMENT ANALYSIS OF THERMAL DRYER ATMOSPHERIC DISCHARGE IS GIVEN BELOW IN MICROGRAMS PER CUBIC METER

PYR S	.1300E+06	ORG S	.3215E+05	SUL S	3572.	N	.8288E+05
AS	6.112	CD	.5332E-01	PB	7.951	HG	2.767
FE	2146.	MN	9.479	BE	9.288	SE	10.71
AL	2889.	ZN	17.01	NI	2.055		

CALCULATED AMOUNT OF COMBUSTION AIR IN MSCF/MILLION BTUS IS GIVEN BELOW

11.06

TOTAL MSCF OF FLUE GAS AND LBS OF ASH RESPECTIVELY FROM THE COMBUSTION PROCESS ARE GIVEN BELOW

11.44                      9.389

TRACE ELEMENT ANALYSIS IN MICROGRAMS PER CUBIC METER FOR FLUE GAS AND WEIGHT FRACTIONS FOR ASH STREAMS RESPECTIVELY ARE GIVEN BELOW. ASH INCLUDES FLY ASH FROM PRECIPITATOR.

PYR S	0.1180E+07	0.0000
ORG S	0.5077E+06	0.0000
SUL S	0.3242E+05	0.0000
N	0.1309E+07	0.0000
AS	27.34	0.1231E-03
CD	0.1930	0.5070E-06
PB	43.99	0.9228E-04
HG	23.52	0.2492E-06
FE	5885.	0.1133
MN	15.73	0.2336E-03
BE	22.59	0.1543E-04
SE	29.44	0.1342E-04
AL	5300.	0.1319
ZN	88.43	0.3594E-03
NI	0.0000	0.1010E-03

SULFUR COMPOSITION OF FLUE GAS IN LBS SO<sub>2</sub>/MILLION BTUS AND MICROGRAMS PER CUBIC METER RESPECTIVELY ARE GIVEN BELOW

2.455                      0.1722E+07

NOX, PARTICLE, HYDROCARBON, AND CO MICROGRAMS PER CUBIC METER FOR FLUE GAS ARE GIVEN BELOW

0.9337E+06              0.1054E+06              0.1556E+05              0.5187E+05

SULFUR COMPOSITION OF THERMAL DRYER EMISSION IN LBS SO<sub>2</sub>/MILLION BTUS CLEANED COAL AND MICROGRAMS PER CUBIC METER ARE GIVEN BELOW

0.3970E-01              0.3315E+06

MICROGRAMS PER CUBIC METER OF NOX, PARTICLES, HYDROCARBONS, AND CO IN THE THERMAL DRYER EMISSION ARE GIVEN BELOW

0.1286E+06              0.2706E+05              2143.                      7145.

ABOVE CONCENTRATIONS FOR PARTICLES ASSUME 99% COLLECTION EFFICIENCY  
OK  
BYE

APPENDIX B

ADDITIONAL FORMULAE FOR DEVELOPING  
ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC's)



## APPENDIX B

### ADDITIONAL FORMULAE FOR DEVELOPING ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC's)

There are additional approaches to predicting possible health/ecological problems associated with coal cleaning activities. Two representative formulae are provided. Formulations and brief rationales are presented.

#### Formulae for International Commissions on Radiological Protection<sup>(3)\*</sup>

These formulae were developed for estimating maximum permissible concentrations of radioactive materials to which man could be exposed via inhalation or ingestion. Other general comments are available in the text (Section 5.5.1.1).

Maximum-permissible-concentration formulae for air- and water-borne harmful materials, particularly radionuclides, are:

(1) For air:

$$(\text{MPC})_a = \frac{10^{-7} q f_2}{T f_a (1 - e^{-0.693t/T})} \mu\text{Ci}/\text{cm}^3$$

- where  $(\text{MPC})_a$  = maximum permissible concentration in air  
 $q f_2$  = burden of the radionuclide in the critical body organ ( $\mu\text{Ci}$ )  
(where  $q$  = total radionuclide in the body and  $f_2$  = the fraction in a particular organ)  
 $T$  = effective half-life (days)  
 $f_a$  = fraction of inhaled radionuclide reaching the organ of reference  
 $t$  = period of exposure (days)  
Other values are constants.

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\* Reference (3), Section 5.0.

(2) For water:

$$(\text{MPC})_w = \frac{9.2 \times 10^{-4} qf_2}{Tf_w(1-e^{-0.693t/T})} \mu\text{Ci}/\text{cm}^3$$

where  $(\text{MPC})_w$  = maximum permissible concentration in water

$qf_2$  = burden of the radionuclide in the critical body organ ( $\mu\text{Ci}$ )

$T$  = effective half-life (days)

$f_w$  = fraction of that taken into the body by ingestion that is retained in the critical organ

$t$  = period of exposure (days)

Other values are constants.

The rationale for the formulae follows:

- (1) Radioactive material is taken into the critical body organ at a rate of  $P \mu\text{Ci}/\text{day}$ , where  $P$  = intake.
- (2) Biological elimination from critical organs follows a simple exponential law.
- (3) Allowable concentrations are to be calculated for occupational and continuous exposure. Occupational exposure occurs at the rate of 40 hours per week and 50 weeks per year for a continuous work period of 50 years. Continuous exposure occurs at the rate of 168 hours per week. For continuous occupational exposure, the MPC values should be divided by  $2 \times 365/(5 \times 50) = 2.92$  except for submersion (external to the body) where they should be divided by  $3 \times 365/(5 \times 50) = 4.38$ . These values are further explained on page 16 of the reference.
- (4) MPC values based on a critical organ are set by requirements that the dose rate after 50 years of occupational exposures shall not exceed:
  - (a) 3 rems for the gonads or the total body during any period of 13 consecutive weeks.
  - (b) Average RBE dose to the skeleton due to a body burden of  $0.1 \mu\text{Ci}$  of  $\text{Ra}^{226}$  when the effective RBE dose delivered

to the bone from internal or external radiation during any 13-week period was averaged over the entire skeleton.

- (c) 4 rems in any 13-week period or 15 rems in one year for any single organ except the gonads, bone, skin, and thyroid; 8 rems in a 13-week period or 30 rems in one year for skin and thyroid.
- (5) During a 50-year exposure period, equilibrium is reached for the majority of radionuclides because effective half-life is short compared to this work period.
- (6) The average breathing rate is  $10^7 \text{ cm}^3$  of air per 8-hour work day (one-half of the air breathed in 24 hours -  $2 \times 10^7 \text{ cm}^3$ ).
- (7) The average rate of water consumption is  $1100 \text{ cm}^3$  per 8-hour work day (one-half of the water consumed in 24 hours -  $2200 \text{ cm}^3$ ).
- (8) Chemical toxicity is not generally considered in estimating the body burden or MPC values.
- (9) For bone-seeking radionuclides such as  $\text{Sr}^{90}$ ,  $\text{Pu}^{239}$ , etc., which emit significant amounts of particulate radiation, the estimate is based on a comparison with  $\text{Ra}^{226}$  and daughter products.
- (10) For non-bone-seeking radionuclides, the MPC and body burden values are set to limit the weekly RBE (relative biological effectiveness) dose received by the various organs of the body.

Formulae for CUMEX  
(Cumulative Exposure) Index (4)\*

CUMEX is a site-specific hazard assessment based on relationships among media and biota. The index relates the concentration of the pollutant in the medium to its concentration in a biological target. Other comments on this formula are available in Section 5.5.1.2.

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\* Reference (4), Section 5.0.

The basic CUMEX formulae are:

(a) For air:

$$C_A^* = \frac{Q_L}{(V_A f_a + f_{AF} M_F f_w + f_{AW} V_W f_w + k f_b) \tilde{R}},$$

where  $C_A^*$  = CUMEX index for airborne effluent with air as the sampling medium

$Q_L$  = acceptable organ burden limit

$V_A$  = breathing rate of reference individual (cm<sup>3</sup>/day)

$f_a$  = fraction of inhaled pollutant deposited in reference organ

$f_{AF}$  = transfer coefficient from air to food

$M_F$  = mass consumption rate of food (g/day)

$f_w$  = fraction of ingested pollutant reaching reference organ

$f_{AW}$  = transfer coefficient from air to water

$V_W$  = volume consumption rate of drinking water (ml/day)

$k$  = partition coefficient for pollutant between air and blood (μg/ml per μg/cm<sup>3</sup>)

$f_b$  = fraction of pollutant in blood that is deposited in the reference organ

$\tilde{R}$  = cumulative retention to time, T, of pollutant in reference organ (days).

(b) For water:

$$C_W^* = \frac{Q_L}{(f_{WF} M_F f_w + V_W f_w) \tilde{R}},$$

where  $C_W^*$  = CUMEX index for a liquid effluent with water as the sampling medium

$Q_L$  = accepted organ burden limit

$f_{WF}$  = transfer coefficient from water to food

$M_F$  = mass consumption rate of food (g/day)

$f_w$  = fraction of ingested pollutant reaching the reference organ  
 $V_w$  = volume consumption rate of drinking water (ml/day)  
 $\tilde{R}$  = cumulative retention to time, T, of pollutant in reference organ (days).

When both effluent (air and water) types are present,

$$\frac{C_A}{C_A^*} + \frac{C_W}{C_W^*} = 1$$

where  $C_A$  = concentration of the pollutant in air ( $\mu\text{g}/\text{cm}^3$ )

$C_W$  = average concentration of the pollutant in drinking water ( $\mu\text{g}/\text{ml}$ )

$C_A^*$  = CUMEX index for airborne effluent with air as the sampling medium

$C_W^*$  = CUMEX index for a liquid effluent with water as the sampling medium.

The rationale for CUMEX follows:

- (1) CUMEX indices can be determined practically if one knows in detail source emission characteristics, environmental transport process, and biological effects.
- (2) Exposure, dose, or concentration limit depends upon the knowledge of biological effects.
- (3) If relationships among environmental compartments are understood, measurements in a particular sampling medium (air, water, food) along with transport models can suffice to assess human intake.
- (4) Any estimation of total pollutant intake by humans and resulting health effects must include contributions from all possible routes of exposure.
- (5) For the third equation, measurements in at least two sampling media, along with transport models, will be necessary to assess total human intake if there is more than one effluent type.

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16. ABSTRACT <b>The report describes the development of criteria for assessing environmental pollutants associated with coal cleaning processes. The primary problem concerns emissions of pollutants to all three media--air, water, and land--and assessing their effects on humans and the environment. Pollutants associated with coal cleaning are primarily inorganic compounds associated with the ash fraction. Lists of potential pollutants from coal cleaning and utilization, containing hundreds of entries, have been proposed. Selected for investigation were 51 elements and 23 substances or groups of substances. The major criterion for ranking the importance of any pollutant is the relationship between its expected environmental concentration and the maximum concentration which presents no long-term hazard to humans or biota. Environmental concentrations depend on emission rates and the effects of physical transport and dispersion. Although these data will ultimately come from field measurements, for now they must be estimated. Methodology for these estimates are reviewed; the methodology is well developed and little further development appears necessary. Ecological transport and distribution is much less well developed: investigation shows large data gaps for many elements and species. Illustrative data are presented for eight of the more important trace elements.</b>		
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