# Hazardous and Toxic[1] Air Pollutants

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*Abstract* Background and current state of knowledge with regard to hazardous and toxic air pollutants are reviewed. Secondary pollutants formed from the interaction of primary pollutants are likely to be the major hazard. Their formation and biological effects are discussed. The need for a uniform strategy and a realistic cost/risk/benefit analysis of the problem is pointed out.

For the purposes of this paper, "Hazardous and Toxic" air pollutants are defined as those pollutants other than the six "criteria" pollutants that are potentially hazardous and/or toxic. The "criteria" pollutants are sulfur oxides, nitrogen oxides, carbon monoxide, particulates, hydrocarbons, and photochemical oxidants. Ambient air standards for these criteria pollutants have already been established by the U.S. Environmental Protection Agency (EPA) with approval by congressional action (U.S. Environmental Protection Agency, 1971*a*). In addition, standards of performance for several of these criteria pollutants have been established for new stationary sources (EPA, 1971*b*, 1974).

Particulate matter is defined as "any finely divided liquid or solid material, other than combined water, as measured by method 5" (EPA, 1971*b*). Method 5 for the measurement of particulate matter is defined in the December 23, 1971, *Federal Register.*

With this definition, it should be obvious, that particulate matter may consist of hundreds, or even thousands, of individual substances that may have harmful biological effects. It should also be evident that the degree of

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potential biological harm brought about by "particulates" is due not to the particulates *per se* but to their composition and "respirability" or particle size. To determine the total environmental impact of a process, it is therefore necessary to know the degree to which respirable particulates are emitted and their composition.

Particulates are of two types: primary and secondary. Primary particulates are emitted directly by stationary or mobile sources. Secondary particulates are formed in the atmosphere by the reaction of primary pollutants under the influence of such factors as water vapor, ultraviolet radiation, ozone, oxygen, and ammonia. These secondary particulates are generally very fine particles in the aerosol class. The distinction between aerosols and larger particles is not clear-cut. However, aerosols are defined as particulate matter, liquid or solid, of sufficiently small aerodynamic diameter to exist as a relatively stable suspension in air. Generally aerosol particles are in the size range of 0.01 to 10-20 $\mu$m (micrometers). Fine or "respirable" particulates are considered to be those particles less than 3 $\mu$m in size.

Many types of specific materials have been identified in the atmosphere either as contained in aerosols or present in gaseous form, and the biological hazards of many of these have been recognized. National emission standards have already been set by the EPA on asbestos, beryllium, and mercury (EPA, 1973). Hence there is real concern with regard to specific hazardous pollutants, their emission rates, and their specific biological activity.

This concern is well founded. It has been estimated (*Science*, 1974) that the number of known compounds is approximately two *million*, and no more than 6000 have been tested for carcinogenicity. Of this number, only half have been adequately tested. To quote the National Cancer Institute:

> The NCI, working mainly through outside contacts, manages to screen about 200 chemicals a year for carcinogenicity. But as yet there is no systematic way to screen new chemicals before they become part of the environment; indeed, Federal regulators have no way of knowing which of the quarter *million* new substances synthesized each year will go into production.

Unfortunately, epidemiological studies, though extremely useful, are always "after the fact." Nevertheless, on the basis of such epidemiology, followed by biological testing, in 1974 the Occupational Safety and Health Administration (OSHA) set standards for 14 known carcinogenic materials (Occupational Safety and Health Administration, 1974).

Compounds in the atmosphere which are carcinogenic, mutagenic, teratogenic, and neurotoxic have been identified. Additional substances are systemic poisons, materials which aggravate asthma, and those that produce skin

rashes, eye irritation, and vegetation damage. There are smog producers and compounds that are thought to be producing long-term biospheric damage, causing temperature changes (Hobbs, Harrison, and Robinson, 1974), and destroying the protective layer of ozone in the upper atmosphere (Cicerone, Stolarski, and Walters, 1974). New and potentially dangerous substances are being identified virtually every month.

This alarming array of materials that are being emitted, coupled with epidemiological evidence of the rising incidence of certain diseases such as cancer, has justifiably caused great concern on the part of the federal government and the general public. It is the job of EPA and numerous research agencies throughout the world to identify which emissions are harmful. It is the job of the Industrial Environmental Research Laboratory of EPA to assist in the development of the proper control technology within the limits of its resources.

As stated earlier, the biological effects of particulate matter are a function of their respirability and chemical composition. Figure 1 is a simplified diagram of the respiratory tract. Note that from the nasal cavity down to the extreme lower portions of the lungs, there is more and more branching of the passages; this results in a constant reduction in air velocity.

When air containing an aerosol or fine particulate matter is inhaled, the aerosols are deposited in the respiratory system by three primary mechanisms: (1) inertia, (2) gravity, and (3) diffusion. For larger particles, inertia is the primary deposition mechanism, and this usually occurs in the nasal and tracheal passages where the air velocity is relatively high.

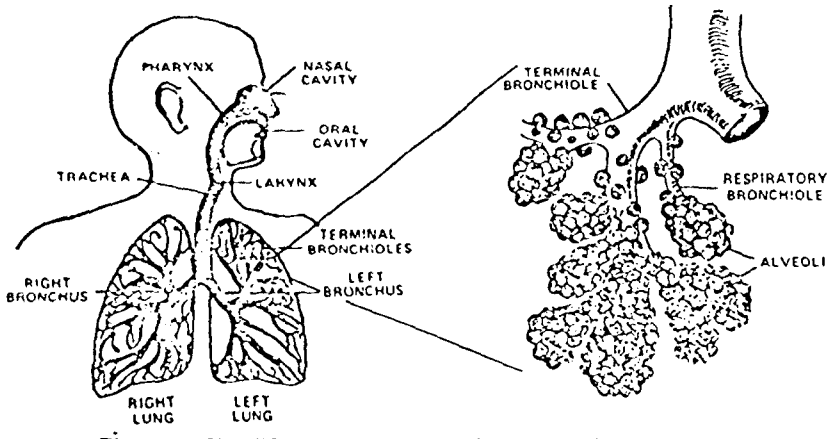


Figure 1. Simplified diagram of the human respiratory tract.

Gravity settling occurs where the air velocity is much lower and depends on the aerosol diameter, density, and medium viscosity. Diffusion occurs as the aerosols approach the size of the molecules of the medium in which they are immersed, and is important in the pulmonary air spaces for aerosols of less than 0.5 $\mu$m in diameter.

Figure 2 shows the fractional deposition of particles at various depths within the human lung (Mercer, 1973). Thus at 3.0 $\mu$m, 80% of the particles are deposited deep in the lungs i.e., in the alveolar ducts and sacs. These represent the more hazardous particles, and particles smaller than 3.0 $\mu$m are called respirable particulates.

Such particles are dangerous not only because of their deep penetration into the lungs, but also because certain hazardous materials become concentrated on fine particulates (Natush and Wallace, 1974). Figure 3 shows how certain element concentrations have been found to vary as a function of particle size on a sample of fly ash. In a combustion or high-temperature process in which the emissions are cooled, the elements with higher boiling points apparently condense selectively on high surface area particles, which are the respirable ones. There is thus a double danger in fine particulates: They penetrate deeper into the respiratory tract, and they may contain a higher concentration of

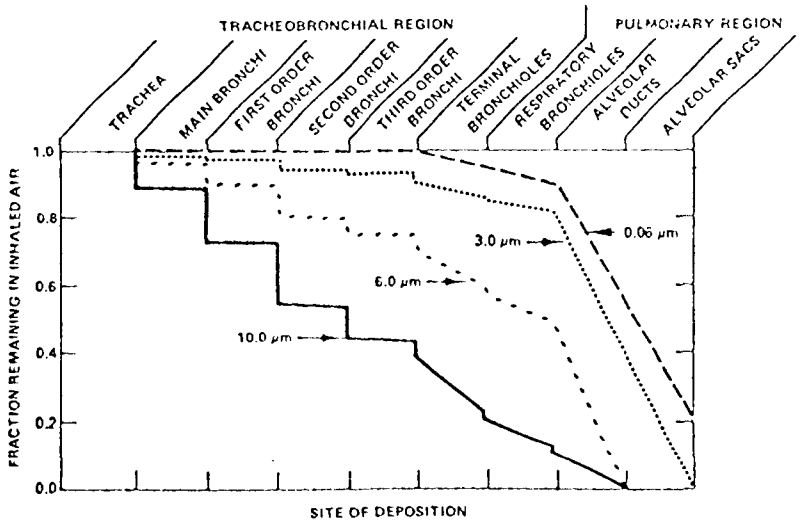


Figure 2. Lung deposition, during inspiration, of particulates that enter the trachea.

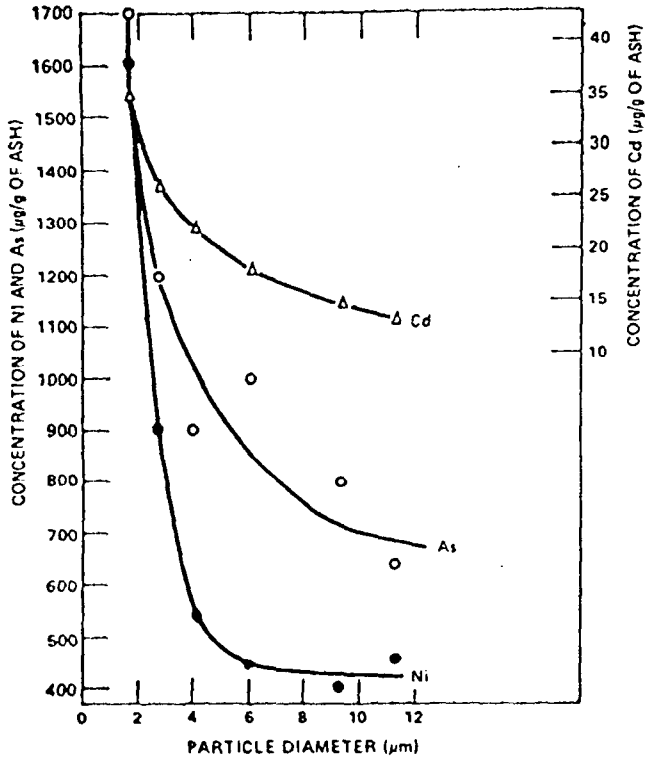


Figure 3. Dependence of concentration of some elements on particle size.

toxic or hazardous materials in addition to the possible toxicity of the base material on which they are adsorbed.

For aerosols deposited in the pulmonary region, four physiobiological mechanisms may occur (Hatch and Gross, 1964):

1. They can be transported to the mucous blanket of the upper respiratory tract and from there, by action of the cilia, discharged along with aerosols deposited in that region. In this case they generally find their way to the stomach.
2. They can be transported to the lymph nodes draining the lungs.

3. They can be sequestered within the lungs by a tissue reaction giving rise to a pathological condition known as pneumoconiosis.
4. They can dissolve and pass into the blood stream or remain bound to the tissue in the lung.

There are gaseous substances emitted into the atmosphere, such as acrolein, hydrogen cyanide, and sulfur dioxide, which tend to paralyze the cilia of the upper tract and impair the lung clearance mechanisms (National Academy of Sciences, 1942) as well as other defense mechanisms.

As indicated above, pollutants are generally classified into two types: primary and secondary. Primary pollutants are emitted by the pollutant sources directly into the atmosphere. Secondary pollutants are formed in the atmosphere either by reaction of the primary pollutants or by reaction of the primary pollutants with natural pollutants already present in the atmosphere.

Secondary pollutant formation is a vastly complex series of mechanisms, many of which are not fully understood. Many of these reactions occur under the influence of ultraviolet radiation, water vapor, oxygen, and ozone. Some of the complex interaction of pollutants involving both adsorption and reaction, together with some of the biospheric effects, are shown in Figure 4.

Most of the fine or respirable particulates or aerosols in the atmosphere are formed from these types of reactions. It has been estimated that a major portion of the synthetic fine particulate pollutants are of the secondary type, i.e., formed from the reaction products of primary pollutants or from the reaction of primary pollutants with natural pollutants in the atmosphere (C. T. Ripberger, EPA/IERL, personal communication).

For purposes of simplification, I have attempted to classify airborne pollutants into broad categories as follows:

1. "Criteria" pollutants
   a. $SO_x$
   b. $NO_x$
   c. CO
   d. Total particulates
   e. Photochemical oxidants
2. Polynuclear aromatic hydrocarbons (PNAH)
3. Trace elements
4. "Permanent" gases
   a. Chlorofluoromethanes
   b. Carbon dioxide, etc.
5. Pesticides

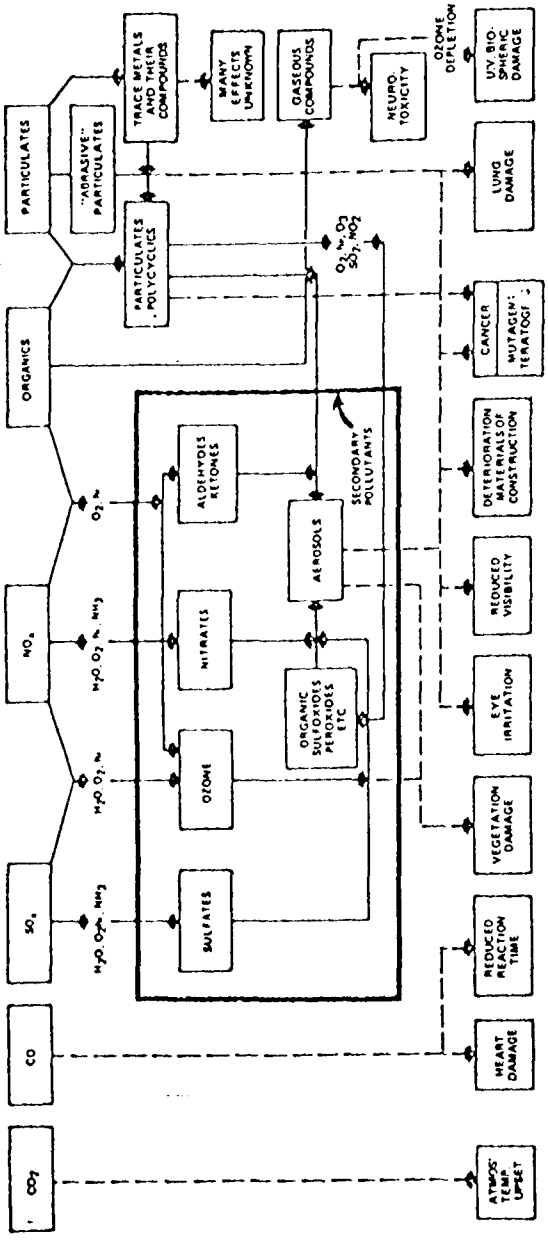


Figure 4. Interrelationship of primary and secondary pollutants and their effects (indicated by dashed lines).

6. "Abrasive" particulates
   a. Silica
   b. Asbestos, etc.
7. Miscellaneous. Examples:
   a. Nitrosomines
   b. Polychlorinated biphenyls (PCB)
   c. Sulfates
   d. Nitrates
   e. Aldehydes, ketones, etc.
   f. Ozone

The criteria pollutants, already discussed, are all primary pollutants. The next class, the polynuclear aromatic hydrocarbons, may be either secondary or primary pollutants, and are largely absorbed on particulate matter. Many of these are carcinogenic, and some are mutagenic and teratogenic.

The next class comprises the trace elements, many of which are toxic, such as arsenic, beryllium, cadmium, magnesium, and chromium. These are usually present as inorganic salts adsorbed on particulate matter from the emitting source. As many as 60 trace elements have been identified in coal and coal combustion products.

The "permanent gases" are those pollutants that have a relatively long life: these include carbon dioxide and the chlorofluoromethanes or freons. These latter compounds are said to accumulate in the stratosphere and, by a chain reaction, destroy the ozone layer. Carbon dioxide, though nontoxic in the usual sense of the word, is said by some scientists to be causing a gradual global temperature change.

The pesticides are those toxic materials that are deliberately sprayed into the atmosphere by humans, and many of these may have adverse biological effects on humanity as well as insects. There have been recent congressional hearings on some of these, such as aldrin and dieldrin.

The so-called abrasive particulates include silica and asbestos, although this category is probably misnamed. The health effects are many and varied and the mechanisms are not fully understood. Silicosis is a commonly known condition, and, in addition to asbestosis, a tumorous condition of the lung known as mesothelioma is associated with asbestos.

The miscellaneous group includes nearly all reaction products from primary pollutants, the more important of which are the sulfates, nitrates, and nitrosomines.

The effects of pollutants are:

1. Carcinogenesis
2. Mutagenesis
3. Teratogenesis
4. Neurotoxicity
5. Ciliastasis
6. Cytotoxicity
7. Silicosis
8. Pneumoconiosis
9. Heart damage
10. Delayed reaction time
11. Smog production
12. Biospheric temperature upset
13. Ozone destruction in stratosphere
14. Ozone production
15. Vegetation damage
16. Destruction of materials of construction
17. Lesser effects
    a. Odor
    b. Tearing of eyes
    c. Rashes
    d. Allergens, etc.

Some of these are the consequence of both primary and secondary pollutants, many of which have already been discussed.

The vast complexity of pollution mechanisms means that control of many pollutants is very difficult. Just accumulating a sufficient data base to make rational decisions is a tremendous undertaking. To further complicate matters, biological response as a function of dose is not a clear-cut matter, making it difficult in many cases to set standards.

Let us consider, for example, the first three pollutant effects given above, namely, carcinogenesis, mutagenesis, and teratogenesis. Carcinogenesis, of course, means cancer-causing; mutagenesis is a change in genetic structure, and the condition is therefore transmittable from generation to generation; teratogenesis is the formulation of nontransmittable birth abnormalities, ranging from slight malfunctions or malformations to the production of monsters.

In the case of many toxic substances, acute effects on animals can be observed as a function of dose, and a threshold limit value (TLV), i.e., a concentration below which no observable toxic effects occur, can be established. Many scientists feel that there is no "safe limit" for carcinogens,

mutagens, or teratogens, and reliable short-term bio-assay techniques are lacking.

Long-term tests require 18-36 months to run, and extrapolation to zero response is not feasible. This is illustrated in Figure 5, in which a typical dose-response curve is plotted. An enormous number of subjects would be required to obtain statistically significant results at low doses. The possible uncertainty in extrapolating to zero response is indicated by the three dashed segments of the curve.

At the moment it appears that the best one can do is to establish acceptable limits based on risk/benefit ratios, i.e., to establish standards such that the risk will be one in $10^6$ or $10^7$ that anyone exposed to the dose may develop, for example, cancer. This was pointed out recently by the National Cancer Institute, and this group urged that standards for carcinogens be set on this basis (*Science*, 1974).

There is still another complicating factor in the overall picture of pollution and human health, and that is the synergistic effect of many pollutants, both natural and synthetic. For example, the well-known carcinogen benzo alpha

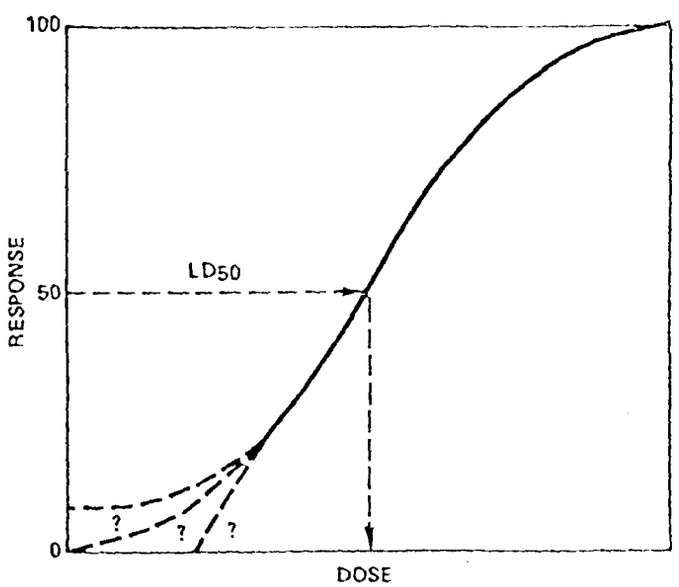


Figure 5. Plot of a typical dose-response curve, illustrating the difficulty of determining threshold limits.

pyrene (BAP) is not a potent carcinogen in the human lung per se (Hann, Nettesheim, and Gilbert, 1970). However, when adsorbed on otherwise innocuous iron oxide (hematite), it becomes extremely potent (Fauldz, 1957; Kuschner, 1968; Saffioti, Cefis, and Kolb, 1968). Similarly, $SO_2$ acts as a promoter for some polynuclears, transforming them into potent carcinogenic materials.

Some of the air pollutants that have been found, their sources, and typical concentrations (in 1971) are shown in Table 1. The difference between rural and city concentrations is readily apparent.

Just what is EPA doing to decrease pollution of the environment from hazardous and toxic materials? At IERL our primary goal in the past has been to develop the technology for the control of $NO_x$, $SO_x$, particulates, CO, hydrocarbons, and photochemical oxidants, i.e., the "criteria" pollutants. Since these are precursors of more toxic secondary pollutants, control of these emissions is still our primary aim. The following is a condensed outline of the program.

1. Control of $NO_x$
   a. Study of precursors and mechanisms
   b. Development of improved combustion techniques
   c. Demonstration units
2. Control of $SO_x$
   a. Development of stack gas scrubbing systems
   b. Precleaning of fuels
      (1) Mechanical cleaning of coal
      (2) Chemical cleaning of coal
      (3) Oil desulfurization
   c. Emission inventories
   d. Demonstration units
3. Control of particulates
   a. High-temperature clean-up (dry)
   b. Low-temperature clean-up
      (1) Dry
      (2) Wet (venturi, charged droplets, etc.)
   c. Emission inventory
   d. Demonstration units
4. Photochemical oxidants (by hydrocarbon control)
   a. Equipment specifications
   b. Emission inventory
   c. Demonstration units

Table 1

Estimated Pollutant Concentrations (1971)

| POLLUTANT | PRINCIPAL SOURCES | TYPICAL CITY CONCENTRATION, PPM | TYPICAL RURAL CONCENTRATION, PPM |
|---|---|---|---|
| CARBON MONOXIDE | AUTO EXHAUST | 5.0 | 0.1 |
| SULFUR DIOXIDE | OIL BURNERS | 0.2 | 0.002 |
| NITRIC OXIDE | COMBUSTION | 0.2 | 0 002 |
| NITROGEN DIOXIDE | COMBUSTION | 0.1 | 0.001 |
| OZONE | ATMOSPHERIC PHOTO-CHEMICAL REACTIONS | 0.3 | 0.010 |
| METHANE | NATURAL GAS, DECAYING ORGANIC MATTER | 3.0 | 1.4 |
| ETHYLENE | AUTO EXHAUST | 0.05 | 0.001 |
| ACETYLENE | AUTO EXHAUST | 0.07 | 0.001 |
| PEROXYACETYL NITRATE | ATMOSPHERIC PHOTOOXI-DATION OF OLEFINS | 0.03 | 0.001 |
| OLEFINS WITH THREE OR MORE CARBONS | AUTO EXHAUST | 0.02 | 0.001 |
| TOTAL HYDROCARBONS EX-CLUDING METHANE | AUTO EXHAUST | 2.0 | 0.005 |
| AMMONIA | DECAYING ORGANIC MATTER | 0.010 | 0.010 |
| HYDROGEN SULFIDE | DECAYING ORGANIC MATTER | 0.004 | 0.002 |
| FORMALDEHYDE | INCOMPLETE COMBUSTION, ATMOSPHERIC REACTIONS | 0.05 | 0.001 |

More and more emphasis is now being placed on control of hazardous and toxic materials, which include materials deposited on the so-called respirable particulates. A condensed outline of the current program in this area is as follows:

1. "Respirable" particulates
   a. Emission inventory
   b. Development of size classification devices
   c. Characterization by particle size
   d. Chemical analyses
   e. Bio-assays
   f. Development of control equipment
2. Source assessment
   a. Chemical processes
      (1) Hazardous and toxic emission (chemical analysis, bio-assays)
      (2) Impact factors (population density, emission rates, etc.)
      (3) Process studies for control of emissions
      (4) Recommendations
   b. Fuel combustion processes–ditto
   c. Metallurgical processes–ditto
   d. Development of industrial process catalogue
3. Total environmental assessment guidelines

Obviously a program of this magnitude draws on many disciplines, many of which are outside the expertise of IERL personnel. We are very fortunate in having located within the same building, and/or in the same area, EPA's Human Studies Laboratory, the Experimental Biology Laboratory, the Chemistry and Physics Laboratory, and the Office of Air Quality Planning and Standards (OAQPS). Located nearby is the National Institute of Environmental Health Sciences (NIEHS), a branch of the Department of Health, Education and Welfare.

These organizations are of immense assistance in our control system program in helping us attain our goals. This assistance is rendered in such areas as development of new analytic techniques, new short-term bio-assays, biological effects of pollutants, and advanced sampling techniques.

IERL is not only concerned with existing industrial complexes and the pollution that occurs as a result thereof. We are also vitally concerned with emerging technology and the impact that such technology is likely to have on the environment. Some of the emerging technologies that are of concern to IERL are:

1. Coal gasification
   a. Low-Btu gas
   b. High-Btu gas
2. Coal liquefaction
3. Utilization of shale oil
4. Utilization of municipal solid waste
   a. Gasification
   b. Co-firing in utility boilers
5. Production of new chemicals
6. Pyrolytic processes for the production of clean fuels
7. Fuel cells

Nothing worth accomplishing has ever been easy, and we fully recognize the difficulties involved in setting standards for the control of pollutants that present a biological threat to humanity. Yet we *must* do this to provide a healthier environment for future generations.

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