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COMPREHENSIVE ASSESSMENT OF TOXIC EMISSIONS FROM COAL-FIRED POWER PLANTS

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"Comprehensive Assessment of Toxic Emissions
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This paper briefly describes both recent and ongoing studies being conducted to assess hazardous and toxic substances from a variety of coal-fired electric utility power generation and environmental control subsystems. Also, current and future U.S. Department of Energy plans to augment these assessments will be addressed.

INTRODUCTION

The trace elements associated with the mineral matter in coal and the various compounds formed during coal combustion have the potential to produce air toxic emissions from coal-fired electric utilities. The recently enacted Clean Air Act Amendments (CAAA) contain provisions that will set standards for the allowable emissions of 190 hazardous air pollutants (HAPS). These 190 air toxics indicated in Table 1 can be associated with any number of source categories that emit pollutants to the environment. Many of these HAPS could possibly be emitted from coal-fired electric generating stations. Coal-fired electric utility boilers will be studied by the EPA to determine if regulation is appropriate and necessary.

Title III, the Hazardous Air Pollutants section of the CAAA, requires the EPA to determine stationary source categories that have the potential to emit any of the 190 HAPS listed in the act. Coal-fired electric utilities are contained in a draft list of 750 sources that the EPA has already developed. The EPA will designate as major sources those stationary sources that could emit 10 tons per year of any single HAP or 25 tons per year of a combination of HAPS. After November 15, 1991, all major sources must be regulated over a 10-year period, according to a schedule provided in the CAAA. Determination of whether or not coal-fired power plants need alternative control strategies for any HAPS emissions that may warrant regulation will be made before November 15, 1993.

Considerable actual HAPS emission data already exist for many of the stationary sources that will be designated as major sources under Title III. In these cases, the EPA will be able to use sound scientific data to prepare regulations. In contrast, a limited data base exists for coal-fired utility boilers. Much of the technical literature concerning toxic emissions from coal combustors consists of calculated values based on test burns under controlled conditions or incomplete material balance studies that related the emissions of trace metals to the inorganic composition of the input coal. Also, there is a high degree of uncertainty concerning much of the data on some of the more volatile components contained in the generated flue gas. For example, results from a literature survey indicated that wet scrubbers may remove anywhere from 20 to 80 percent of the mercury from utility boiler flue gas.

Conventional air pollution control subsystems have the potential to remove many of the air toxic emissions from flue gas generated from the combustion of coal. There is a lack of precise analytical data on the removal of toxics across environmental control devices, such as

electrostatic precipitators, baghouses, and wet limestone scrubbers. However, the relative concentrations of some of the toxic materials could also be increased as a result of using these technologies, or toxics could be formed when chemicals are added to the flue gas stream to increase particulate collection efficiency. Further, some of the more advanced SO_2 and NO_x mitigation technologies involve furnace injection of a sorbent and combustion modification, respectively. To date, little information exists on the effects these advanced technologies have on the amounts of toxic substances formed in the combustion zone.

Efforts are under way to develop a more complete data base on potential HAPS emissions from electric utilities. During the first phase of a two-phase program, the Canadian Electric Association conducted a study to examine air, water, and ash pathways for trace constituents released to the environment from four Canadian coal-fired generating stations. The second phase of the program dealt with the environmental dispersion and biological implications of the release.

The Electric Power Research Institute (EPRI) has begun to assess the emissions from power plants under the PISCES (Power Plant Integrated Systems: Chemical Emission Studies) program. This activity involves the use of a consistent and comprehensive analytical protocol that evaluates all inputs and outputs concerning pollution control and process streams at the utility. To date, the EPRI study has gathered analytical information at six utility sites for 24 of the 190 hazardous pollutants listed in Title III of the CAAA.

The Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE) has two current investigations, initiated before passage of the CAAA, that will determine the air toxic emissions from coal-fired electric utilities. DOE has contracted with Battelle Memorial Institute and Radian Corporation to conduct studies focusing on the potential air toxics, both organic and inorganic, associated with different size fractions of fine particulate matter emitted from power plant stacks. Table 2 indicates the selected analytes to be investigated during these studies. PETC is also developing guidance on the monitoring of HAPS to be incorporated in the Environmental Monitoring plans for the demonstration projects in its Clean Coal Technology Program.

These ongoing DOE air toxic emissions studies, which were initiated before passage of the CAAA, are somewhat limited in scope and therefore cannot provide all the information necessary for Title III considerations and requirements. Consequently, there is a need to expand and broaden these studies so as to increase the technology base on toxic emissions from coal-fired utilities.

RECENT/CURRENT TOXIC EMISSIONS STUDIES

Canadian Electric Association Study

A major toxic emissions study was performed by the Battelle Pacific Northwest Laboratories for the Canadian Electric Association (CEA). The objectives of the CEA-sponsored study were the following:

- Identify release pathways for trace elements in coal-fired generating stations and to quantify the releases.

- Document the accuracy and reliability of various analytical and sampling procedures.

- Identify the effect of operational parameters on the release of trace elements to the environment.

- Determine the effects of trace releases on living organisms.

- Compare the quantity of trace constituent releases from power plants to those from other man-made sources.

- Provide a basis for determining the effectiveness of controls.

The CEA program did not study emissions associated with acid rain. This program dealt strictly with coal-fired power generating stations. The four stations studied and the types of coal used were the following:

- Battle River - Subbituminous C (low-sulfur)
- Poplar River - Lignite (medium-sulfur)
- Nanticoke - Bituminous (low-sulfur)
- Lingan - Bituminous (high-sulfur)

The CEA study was divided into two phases. Phase I work dealt with obtaining and analyzing data pertaining to emissions to the environment and quantifying those emissions and identifying the pathways to the environment. This phase was completed in early 1985. Phase II consisted of work on dispersion in and effects on the environment. Our discussion of the CEA work will be limited to Phase I since this paper is chiefly concerned with identifying and quantifying trace toxic emissions to the environment.

To determine the pathways to the environment a number of streams were sampled and analyzed at each plant. These were the following:

- Feed coal
- Bottom ash
- ESP hopper ash
- Inlet and outlet ash sluice water
- Ash lagoon water
- Stack flue gas
- Flue ash (emitted particulates)
- Miscellaneous, site-specific samples

These materials were sampled for up to 45 elements in addition to polycyclic aromatic hydrocarbons. Material balances were made based on the averages of several runs. Closure to within 20% was found for 37 elements. Elements for which closure was not obtained were fluorine, silicon, phosphorus, cadmium, boron, and mercury.

Some elements become enriched in the flyash as it passes through the system from the furnace to the stack. The elements included boron, zinc, gallium, arsenic, selenium, molybdenum, cadmium, antimony, and lead. Of these, only antimony, arsenic, cadmium, lead, and selenium are on the EPA's HAPS list. Other elements have patterns of enrichment that varied from plant to plant. These included sodium, vanadium, chromium, manganese, cobalt, nickel, copper, barium, and uranium. Of these, chromium, manganese and cobalt are found on the EPA's HAPS list. Most elements were found to be part of the silicate matrix and showed no enrichment patterns. It should also be noted that enrichment was most pronounced in the smallest size particles.

The volatile and gaseous elements were all found to be depleted from the ash and are assumed to be emitted as vapors. These include fluorine, sulfur, chlorine, bromine, and mercury. Chlorine and mercury are on the EPA's HAPS list. Two elements, selenium and arsenic, are not gases but are released to the atmosphere. From 4 to 73% of the selenium in the coal is released while 1 to 9% of the arsenic is released with the flue gas. It is interesting to note that arsenic emissions tended to be inversely proportional to the calcium content of the coal.

Measurements of Polycyclic Aromatic Hydrocarbons (PAH) emissions were obtained at three of the plants. At all three plants, the emission levels were very small and ranged from .15 to .66 grams per hour per megawatt ($\approx$ .17 to .73 lb/hr for a 500 MW plant). The largest single-compound emission found was benzo(a)pyrene. Other relatively high PAH emissions included 9,10-dihydroanthracene, 9-methylanthracene, 9,10-dimethylanthracene, and 1,2-benzofluorene.

The CEA study also investigated the release of radionuclides. There was significant evidence of the fractionation of radionuclides in their movement through the system. Enrichment was found for ^{210}Pb and ^{238}U. Essentially all of the ^{222}Rn is released as a gas. While the concentration of radon in the stack gas is 30 to 90% over ambient, it is quickly diluted to near ambient levels. Over all, the release of all radionuclides is of minimal significance.

Table 3 summarizes the emissions of the elements listed on the EPA HAPS list. The data resulted from measurements at several power plants. These plants use the coals described previously.

EPRI's Field Chemical Emissions Monitoring (FCEM) Project

The EPRI air toxic emissions study is being carried out by Radian Corporation. The objectives of the current study are the following:

- Develop material balances around the combustion system and associated air pollution control equipment.

- Provide a preliminary basis for partitioning around control devices.

- Provide an indication of the long-term, uncontrolled variability for species emitted from a conventional power plant.

This project will involve measuring the quantities of select chemical species at key points in a power plant to close the material balance for those selected chemical substances. The FCEM project is a follow-on to an earlier EPRI project called PISCES. The PISCES project consisted of an exhaustive literature review to obtain as much existing data as possible on the emission of chemical species from power plants. This data was then organized into a data base that contains information on both individual power plants and on the chemical characteristics of various streams within those plants. The PISCES project also served to identify gaps in the existing data on power plant emissions. These data gaps are most prevalent in the category of trace chemical or element atmospheric emissions.

The current FCEM project seeks to eliminate those gaps pertaining to the emission of trace elements from power plants. This will quantify the concentration of select materials in streams leaving the plant. The project will also result in probabilistic concentration profiles for select chemical species.

The sampling and analysis portion will take place at select coal-, oil- and gas-fired conventional power plants (fossil fuel, steam turbine generator). While the end results will be specific to these power plants, they will be selected so as to be representative of a significant number of U.S. power plants. The tests will be made for both organic and inorganic species in both controlled and uncontrolled streams. The specific chemical species, as well as the specific power plants, will be selected to provide a solid baseline for future work. Compounds to be the subject of these analyses are expected to include arsenic, cadmium, chromium, lead, mercury, nickel, selenium, vanadium, zinc, benzene, formaldehyde, chlorides, fluorides, and PAH. Streams to be sampled for a coal-fired unit include feed coal, coal pile runoff, bottom ash, economizer ash, ESP gas inlet and outlet, ESP ash, FGD system inlet, FGD system outlet, stack gas and FGD waste. Appropriate power generation and environmental control subsystems of oil- and gas-fired units will be sampled for comparison of toxic emissions.

The end result of the FCEM project will be reasonably complete emission profiles on trace toxic species from a number of power plants that are representative of many U.S. power plants. This information will be obtainable from the PISCES data base and will serve as the benchmark for further work that needs to be done in quantifying trace emissions from power plants.

Battelle Memorial Institute

Battelle Memorial Institute and its subcontractor Keystone/NEA will make a correlation between air toxics produced by a laboratory combustor and two operating coal-fired electric utility boilers. A characterization of air toxics associated with the surfaces of fine particles and vapor phase constituents of the stack flue gas of the selected coal-fired units will be made. Diluted, cooled flyash particles with adsorbed and condensed material on the surfaces and hot gas flyash particles without a majority of these absorbed and condensed materials will be collected in three size fractions from the stacks. These size fractions are <0.6, 0.6-2.0, and 2.0 - 5 microns.

An innovative source dilution sampler will be utilized to simulate plume cooling and collect the diluted, cooled particles that may have an increased concentration of certain toxic substances. The hot gas samples, particulate and vapor phase, will be collected by EPA Modified Method 5 procedures. The differences in the two samples will provide information on the characteristics of surface layer composition of fine particles, particularly materials of air toxic concern.

Laboratory studies can be more useful under certain circumstances than full-scale studies because of the flexibility to examine emissions from developing pollution control technologies (i.e., furnace and duct sorbent injection, flue gas conditioning, and from various combustion configurations). If possible, the coals used by the two coal-fired electric utilities will be used in the laboratory combustion studies, which will indicate the efficiency of using a well controlled laboratory-scale combustor to simulate emissions from a full-scale unit. Additional results from the Battelle laboratory combustion work will include the further development of more advanced sampling methods for collection of flyash and vapor phase constituents from flue gas. The results will also assist DOE and EPRI in determining which toxic substances to sample in future emissions characterization studies.

Radian Corporation

Radian Corporation will collect size fractionated particles from the stack of a full-scale coal-fired utility boiler and characterize the particles for both bulk and surface chemical composition. The sampling will take place over two different time periods ranging from three to four weeks. This will enable the collection of fine particles during a high-load season (winter) and a lower-load season (spring), and during load swings. Particulate samples will be collected from the stack effluent under both hot stack and dilution-cooled conditions.

A source dilution sampler will be utilized to simulate the cooling and dilution that the flue gases and particles experience while entering the atmosphere at the stack exit. A relationship will be determined between the chemical materials found and the size of particles. Also, an evaluation and subsequent characterization will be performed on the effects of cooling and dilution upon the surface condensation of volatile species. In addition, the carbon content of the particulate matter will be determined in an attempt to correlate any organic compounds found on the dilution-sample particulate with the amount of carbon.

Other considerations within this project include the differences in the potential health impacts of each fraction as a function of particle size and the leachability of the toxic chemicals from the particles.

FUTURE TOXIC EMISSION STUDIES

A collaborative effort has been initiated by the DOE, the Utility Air Regulatory Group (UARG), EPRI, and the EPA to expand the study of hazardous pollutant emissions from utility boilers. This effort will involve measurements at a number of power plants having different boiler designs, NO_x control methods, particulate control devices, and SO_2 removal systems (wet and dry). From these measurements, it is anticipated that the EPA will be able to predict the potential air toxic emissions from coal-fired boilers in 1995 and in the year 2000 (after controls are installed to meet the requirements of the acid rain title of the CAAA). Measurements from plants firing bituminous or subbituminous coal will be used to evaluate the entire range of existing power plant configurations and will form the basis for this study.

The DOE through the Office of Project Management at PETC will issue a solicitation for proposals to assess selected hazardous/toxic pollutants from a number of utilities that utilize different pollution control and process subsystems while burning either bituminous or subbituminous coal. An objective of this solicitation will be to determine the removal efficiencies of pollution control subsystems for these selected pollutants and the concentration of the respective pollutants associated with the particulate fraction of the flue gas stream as a function of particle size. A further objective is to determine mass balances for selected pollutants for a variety of different input and output streams of the power plants and subsequently for the entire power plant.

This solicitation will be announced early this fiscal year. A Commerce Business Daily (CBD) announcement was issued in early October 1991, addressing the solicitation. Attachment 1 is the CBD announcement. The primary goal of this work will be to produce concise, consistent data on the hazardous emissions from a number of coal-fired utilities before December of 1992.

The DOE plans to incorporate monitoring of HAPS in the Environmental Monitoring Plans for projects in the Clean Coal Technology Program. The primary objective is to quantify the mass flow rate of the listed HAPs in stack gases emitted to the atmosphere at Clean Coal demonstration sites. A secondary objective is to quantify the removal of HAPs in gaseous streams across pollution control subsystems. Monitoring would be conducted under both baseline and demonstration operating conditions.

Results from all the DOE studies will provide input to the congressionally mandated study being conducted by the EPA to assess the impacts of the listed HAPs emissions from coal-fired electric utilities, as required in Subtitle III of the CAAA of 1990. In addition, the data will provide a basis for evaluating the potential effects of air toxics regulation on existing pollution control and auxiliary processes being utilized at electric utilities and on the commercialization of technologies demonstrated under the Clean Coal Technology Program.

Table 1. The 190 Hazardous Air Pollutants Listed in Clean Air Act Amendments of 1990

Chemical Name
Acetaldehyde
Acetamide
Acetonitrile
Acetophenone
2-Acetylaminofluorene
Acrolein
Acrylamide
Acrylic acid
Acrylonitrile
Allyl chloride
4-Aminobiphenyl
Aniline
o-Anisidine
Asbestos
Benzene (including benzene from gasoline)
Benzidene
Benzotrichloride
Benzyl chloride
Biphenyl
Bis(2-ethylhexyl)phthalate (DEHP)
Bis(chloromethyl)ether
Bromoform
1,3-Butadiene
Calcium cyanamide
Caprolactam
Captan
Carbaryl
Carbon disulfide
Carbon tetrachloride
Carbonyl sulfide
Catechol
Chloramben
Chlordane
Chlorine
Chloracetic acid
2-Chloroacetophenone
Chlorobenzene
Chlorobenzilate
Chloroform
Chloromethyl methyl ether
Chloroprene
Cresols/Cresylic acid (isomers and mixture)
o-Cresol
m-Cresol
p-Cresol
Cumene
2,4-D, salts and esters
DDE
Diazomethane
Dibenzofurans
1,2-Dibromo-3-chloropropane
Dibutylphthalate
1,4-Dichlorobenzene(p)
3,3-Dichlorobenzidene
Dichloroethyl ether (Bis(2-chloroethyl)ether)
1,3-Dichloropropene
Dichlorvos
Diethanolamine
N,N-Diethyl aniline (N,N-Dimethylaniline)
Diethyl sulfate
3,3-Dimethyoxybenzidine
Dimethyl aminoazobenzene
3,3'-Dimethyl benzidine
Dimethyl carbamoyl chloride
Dimethyl formamide
1,1-Dimethyl hydrazine
Dimethyl phthalate
Dimethyl sulfate
4,6-Dinitro-o-cresol, and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
1,4-Dioxane (1,4-Diethyleneoxide)
1,2-Diphenylhydrazine
Epichlorohydrin (1-Chloro-2,3 epoxypropane)
1,2-Epoxybutane
Ethyl acrylate
Ethyl benzene
Ethyl carbamate (Urethane)
Ethyl chloride (Chloroethane)
Ethylene dibromide (Dibromoethane)
Ethylene dichloride (1,2-Dichloroethane)
Ethylene glycol
Ethylene imine (Aziridine)
Ethylene oxide
Ethylene thiourea
Ethylidene dichloride (1,1-Dichloroethane)
Formaldehyde
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexamethylene-1,6-diisocyanate
Hexamethylphosphoramide
Hexane
Hyzadrine
Hydrochloric acid
Hydrogen fluoride (Hydrofluoric acid)
Hydrogen sulfide
Hydroquinine
Isophorone
Lindane (all isomers)
Maleic anhydride
Methanol

(continued)

Methoxychlor
Methyl bromide (Bromomethane)
Methyl chloride (Chloromethane)
Methyl chloroform (1,1,1-Trichloroethane)
Methyl ethyl ketone (2-Butanone)
Methyl hydrazine
Methyl iodide (Iodomethane)
Methyl isobutyl ketone (Hexone)
Methyl isocyanate
Methyl methylacrylate
Methyl tert-butyl ether
4,4-Methylene bis(2-chloroaniline)
Methylene chloride (Dichloromethane)
Methylene diphenyl diisocyanate (MDI)
4,4'-Methylenedianiline
Naphthalene
Nitrobenzene
4-Nitrobiphenyl
4-Nitrophenol
2-Nitropropane
N-Nitroso-N-methylurea
N-Nitrosodimethylamine
N-Nitrosomorpholine
Parathion
Pentachloronitrobenzene (Quintobenzene)
Pentacholorphenol
Phenol
p-Phenylenediamine
Phosgene
Phosphine
Phosphorus
Phthalic anhydride
Polychlorinated biphenyls (Aroclors)
1,3-Propane sultone
beta-Propiolactone
Propionaldehyde
Propoxur (Bargon)
Propylene dichloride (1,2-Dichloropropane)
Propylene oxide
1,2-Propylenimine (2-Methyl aziridine)
Quinoline
Quinone
Styrene
Styrene oxide
2,3,7,8-Tetrachlorodibenzo-p-dioxin
1,1,2,2-Tetrachloroethane
Tetrachloroethylene (Perchloroethylene)
Titanium tetrachloride
Toluene
2,4-Toluene diamine
2,4-Toluene diisocyanate
o-Toluidine
Toxaphene (Chlorinated camphene)
1,2,4-Trichlorobenzene
1,1,2-Trichloroethane
Trichloroethylene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
Trifluralin
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride
Vinylidene chloride (1,1-Dichloroethylene)
Xylene (isomers and mixture)
o-Xylenes
m-Xylenes
p-Xylenes
Antimony Compounds
Arsenic Compounds (inorganic including arsine)
Beryllium Compounds
Cadmium Compounds
Chromium Compounds
Cobalt Compounds
Coke Oven Compounds
Cyanide Compounds[1]
Glycol ethers[2]
Lead Compounds
Manganese Compounds
Mercury Compounds
Fine Mineral Fibers[3]
Nickel Compounds
Polycyclic Organic Matter[4]
Radionuclides (including radon)[5]
Selenium Compounds

NOTE: For all listings above that contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemicals (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

1. X' CN where X = H' or any other group where a formal dissociation may occur. For example, KCN or $Ca(CN)_2$.
2. Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH2CH2)n-OR' where
   n = 1, 2, or 3
   R = alkyl or aryl groups
   R' = R, H, or groups that, when removed, yield glycol ethers with the structure: R-(OCN2CH)n-OH. Polymers are excluded from the glycol category.
3. Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral-derived fibers) of average diameter (1 micrometer or less).
4. Includes organic compounds with more than one benzene ring and boiling points greater than or equal to 100°C.
5. A type of atom that spontaneously undergoes radioactive decay.

Table 2. Compounds and Elements for the Battelle and Radian Air Toxics Studies

Arsenic	Ammonia
Barium	Radionuclides (Ra, Po, U, etc.)
Beryllium	Sulfates
Cadmium	
Chromium	Benzene
Chlorine (as Cl^-)	Toluene
Cobalt	Formaldehyde
Copper	Polycyclic Aromatic Hydrocarbons
Cyanide	
Fluorine (as F^-)	
Lead	
Manganese	
Mercury	
Molybdenum	
Nickel	
Phosphorus (as PO_4^{3-})	
Selenium	
Vanadium	

The other elements associated with Instrumental Neutron Activation Analysis (INAA).

Table 3. Trace Element Releases with the Flue Gas

Element	% of Total Element in Coal Released with the Flue Gas
Chlorine	49 - 99.0
Chromium	0.1 - 8.7
Manganese	0.1 - 1.0
Cobalt	0.09 - 1.5
Arsenic	0.74 - 9.3
Selenium	3.5 - 73.0
Antimony	0.2 - 2.5
Mercury	79.0 - 87.0
Lead	0.2 - 1.4