Carnegie Mellon University
Research Showcase @ CMU

Department of Engineering and Public Policy | Carnegie Institute of Technology

6-1996

Evaluating Trace Chemical Emissions from Electric Power Plants

Michael B. Berkenpas
Carnegie Mellon University

Edward S. Rubin
Carnegie Mellon University, rubin@cmu.edu

Barbara Toole-O'Neil
Electric Power Research Institute

Follow this and additional works at: http://repository.cmu.edu/epp

Part of the Engineering Commons

Published In
Proceedings of ECOS '96 International Symposium-Efficiency, Costs, Optimization, Simulation, and Environmental Aspects of Energy Systems.

This Conference Proceeding is brought to you for free and open access by the Carnegie Institute of Technology at Research Showcase @ CMU. It has been accepted for inclusion in Department of Engineering and Public Policy by an authorized administrator of Research Showcase @ CMU. For more information, please contact research-showcase@andrew.cmu.edu.

EVALUATING TRACE CHEMICAL EMISSIONS FROM ELECTRIC POWER PLANTS

Michael B. Berkenpas and Edward S. Rubin
Center for Energy and Environmental Studies
Carnegie Mellon University
Pittsburgh, PA 15213
Tel=412-268-5897, Fax=412-268-1089, Email=rubin+@cmu.edu

Barbara Toole-O'Neil
Electric Power Research Institute
Palo Alto, CA 94303

ABSTRACT

This paper describes a new computer–based model developed for the Electric Power Research Institute (EPRI) to quantify the flows of chemical species in all gaseous, liquid and solid streams entering and leaving a power plant. User–specified parameters allow the model to be tailored to a variety of power plant configurations and site–specific conditions. A unique feature of the model is that all parameters and input data may be characterized probabilistically so that uncertainties can be analyzed rigorously. Illustrative applications are presented to examine the uncertainty in potential air toxic emissions, the effectiveness of current control measures, and areas for future study.

INTRODUCTION

As a result of the 1990 Clean Air Act Amendments, the potential for regulation of hazardous air pollutants (HAPs) — or "air toxics" — has emerged as a major new environmental concern for U.S. electric utilities. Similar concerns have emerged in other countries, including nations of western Europe. In the United States, 189 chemical species were named in the 1990 Clean Air Act provisions for air toxics. Emissions control is required across a broad spectrum of industrial and other sources emitting 10 tons per year or more of any one of the 189 listed substances, or 25 tons per year or more of any combination of substances. The basis for regulation of industrial sources is the use of "maximum available control technology" (MACT), with further controls required if an unacceptable level of risk to public health remains after MACT is applied. Electric power plants, however, were exempt from the initial provisions of the 1990 air toxics requirements, pending completion of several additional studies by the U.S. Environmental Protection Agency (USEPA). One key study involves an examination of the hazards to public health reasonably anticipated to occur from emissions of HAPs from steam-electric generating units after the imposition of other requirements of the 1990 Clean Air Act Amendments. The U.S. Congress also required USEPA to develop and describe alternative control strategies for hazardous emissions that may warrant regulation, and to promulgate regulations for electric utilities if "appropriate and necessary" after considering the results of the study.

Two additional studies required by the 1990 amendments call for studies of mercury emissions from electric utilities and other sources. One of these studies will define threshold mercury exposure for adverse human health effects. The other study addresses the health and environmental affects of deposition and hazardous air pollutants onto several major water systems of the United States. If the USEPA concludes that further regulation is required because of either of these studies, then electric utilities could again be included in air toxics regulations.

As of the end of 1995, none of the utility-related studies of hazardous air pollutants have been completed, nor has the USEPA drafted any conclusions or recommendations regarding the need to control air toxics emissions from electric power plants. Such recommendations are now expected sometime in early 1996.

HAPs Research Programs

The potential for new regulations limiting the emissions of trace chemical substances from fossil-fueled electric power plants has motivated substantial research and testing over the past several years to better understand and characterize trace species emissions from a variety of power plant systems. Recent efforts have included programs at the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (USDOE), as well as the USEPA. The largest of these

programs to date has been the EPRI program called, Power Plant Integrated Systems: Chemical Emissions Studies (PISCES). Since its inception in 1988, the PISCES program has focused primarily on three areas: (1) compiling a database of information on trace chemical species for conventional fossil fuel power plants, based on publicly available literature; (2) a new program of field testing, initiated in 1990, focusing on chemical substances associated with coal, oil, or gas-fired power plants; and (3) development of a computerized chemical assessment model to predict the multi-media emissions of chemical substances from a wide variety of power plant configurations. This paper focuses on the development and applications of the power plant chemical assessment model, known as the PISCES Model.

THE PISCES MODEL

The purpose of the PISCES Model is to allow utilities to evaluate the performance of a given power plant configuration with respect to multi–media emissions of chemical substances. As depicted in Figure 1, the model provides estimates of the mass flow rates of all solid, liquid and gaseous streams entering and emanating from the plant, including quantitative estimates of all trace species emissions. Coal, oil and gas–fired power plants employing any combination of the technologies listed in Table 1 can be configured for analysis. These technology options cover most of the different power plant configurations found in the U.S. and abroad. Fundamental mass and energy balances are used to compute all system flow rates for the configuration selected, with empirical data employed where necessary, as in the calculation of nitrogen oxide emissions or metal cleaning wastes. All continuous stream flows, such as solid wastes, stack gas emissions, and wastewater treatment effluents are characterized, as well as intermittent stream flows such as boiler cleaning wastes and cooling tower basin sludge.

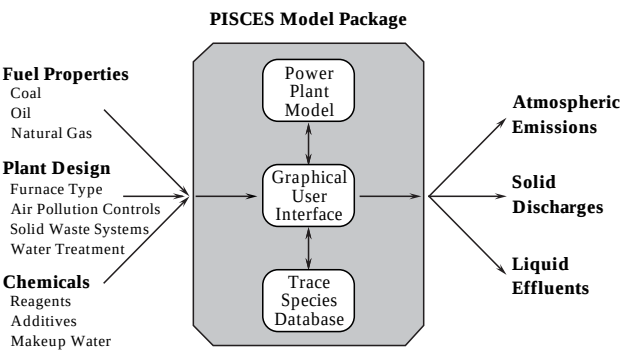

FIGURE 1. SCHEMATIC OF THE PISCES MODEL FRAMEWORK

TABLE 1. CURRENT TECHNOLOGY OPTIONS AVAILABLE IN THE PISCES MODEL

Fuel Characteristics	**Solid Waste Disposal**
• Coal	• Landfill
• Oil	• Ponding
• Gas	• Co–Disposal
Boiler Systems	**Cooling Water System**
• Tangential	• Once–Through
• Wall	• Cooling Tower
• Cyclone	• Pond or Lake
	• Fresh or Saline
NOx Control	
• Low-NOx Burners	**Water Treatment Systems**
	• Plant Makeup Water
Particulate Controls	• Plant Service Water
• Precipitator	• Boiler Makeup
• Fabric Filter	• Condensate Polisher
	• Cooling Tower Makeup
SO_2 Controls	• Tower Slip Stream
• Wet Limestone FGD	• Ash Pond
• Wet Lime FGD	• Settling Pond
• Lime Spray Dryer	• Evaporation Pond

The Graphical Interface

To simplify the use of the model, an interactive graphical interface has been developed. The graphical interface is a separate program that transmits appropriate commands to the power plant model, and receives executed results for display. The complete software package in Figure 1 thus involves interactions between the plant model, the graphical interface and the trace species database, which is described below.

Operation of the model involves three steps: (1) configuring the power plant, (2) setting parameter values, and (3) getting results. These three operations are shown near the top of the screen in Figure 2. Each "button" on the screen can be activated (clicked on) with the computer mouse to call up a more detailed set of options, or to move quickly to any section of the model. The results of an analysis can be displayed in graphical, tabular or diagrammatic form for individual power plant components or the plant as a whole. The interface also provides a capability to import or export all data files for off-line storage, processing or report generation. Additional details on the model design and interface structure are provided elsewhere (Rubin, et al., 1991).

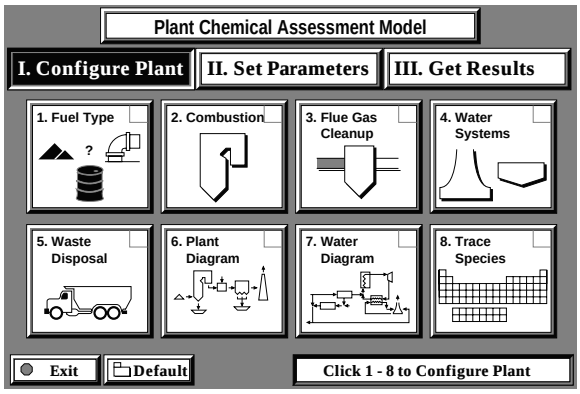

FIGURE 2. PISCES MODEL SCREEN USED TO CONFIGURE A POWER PLANT OR NAVIGATE THROUGH THE MODEL

Probabilistic Capability

A unique feature of the model is its ability to characterize uncertainties probabilistically. Any or all model input parameters can be assigned a probability distribution rather than a single value. The combined effect of all input uncertainties then is reflected in an uncertainty distribution for output parameters of interest obtained using Monte Carlo

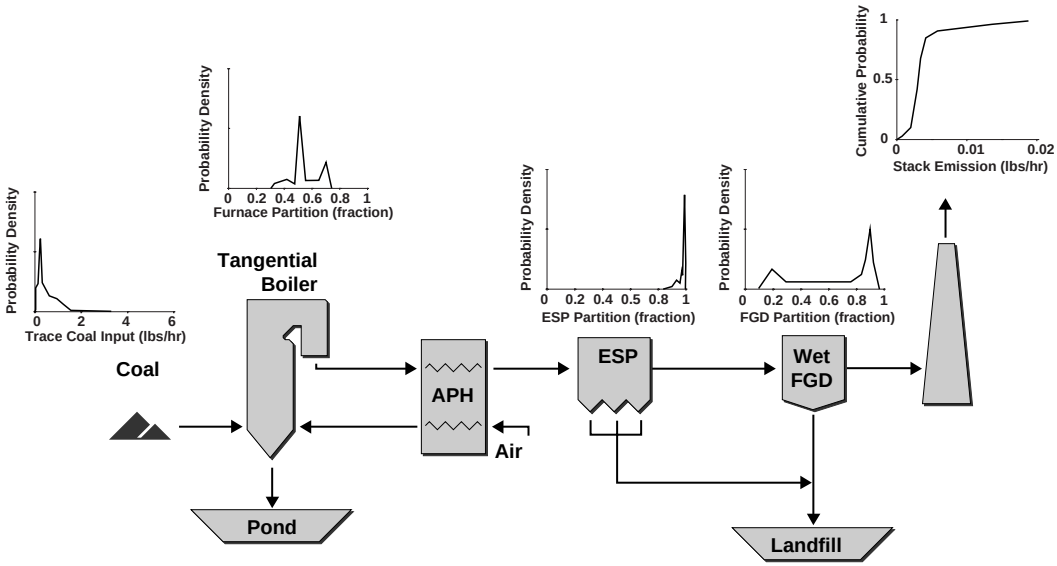

FIGURE 3. EXAMPLE OF PROBABILISTIC PATHWAY IN THE PISCES MODEL

methods. Such distributions give the likelihood of a particular value, in contrast to conventional single–valued estimates. This is especially important for trace species analysis since there is considerable variation in trace species fuel concentrations, as well as in the partitioning of trace substances in the furnace and environmental control devices.

Utilization of the model requires two types of data. One involves specification of plant design parameters such as plant size, fuel composition, capacity factor, and heat rate. These factors affect the mass flow rates of major plant streams. The other type of data, needed to evaluate effluents of trace chemical substances, includes information on the concentration of trace species in all plant inputs streams (including fuel, reagents, water and air), plus performance data characterizing how each chemical constituent in a given stream is "partitioned" or removed in each plant component or environmental control device. For probabilistic analyses, all plant characteristics, chemical species input quantities, and environmental control system performance parameters may be specified as distributions rather than single values. Figure 3 illustrates the probabilistic pathway of trace species emissions for a coal-fired power plant equipped with an electrostatic precipitator and a wet FGD system. The sketch shows input data for the coal properties plus partition factors for the three major plant components affecting stack gas emissions,. Stack emissions are indicated as a cumulative distribution function. This type of result quantifies the likelihood that emissions will reach or exceed a particularvalue. This gives a direct measure of the risk of exceeding an emission limit that may be imposed on a facility.

Trace Species Database

As part of the PISCES program, EPRI has compiled a database of chemical substances found in the streams of conventional fossil fuel power systems (Wetherold, et al., 1995). This database, developed by Radian Corporation, includes extensive information from the technical literature, as well as more recent data from field sampling programs conducted by EPRI and USDOE.

Information from the PISCES Database has been downloaded, parsed and restructured for compatibility with the PISCES Model and interface. Data files have been created for 33 selected trace species of potential concern to utilities (Table 2). Given the current lack of mechanistic models to predict the partitioning of trace species in power plant systems (Benson, et al., 1994), the database files are sorted using available empirical measures such as coal rank, furnace firing method, and technology design characteristics that are relatively coarse surrogates for physical and chemical processes that are known or believed to be important, but which are not well understood or routinely reported.

The most comprehensive datasets for trace species partitioning are for cold-side electrostatic precipitators. Examples from the PISCES database have been reported previously, along with partition factors for tangentially-fired boilers (Rubin, et al., 1993). In general, heavy metals are efficiently removed in an ESP, while volatile or semi-volatile species exhibit greater variability in ESP removal efficiency.

Data for trace species removal in modern FGD systems is less readily available, although progress has been made in

TABLE 2. SELECTED TRACE SPECIES FOR THE PISCES MODEL DATABASE

Ammonia	Chrysene	Mercury
Arsenic	Cobalt	Molybdenum
Barium	Copper	Naphthalene
Benzene	Cyanide	Nickel
Benzopyrene	Fluoride	Phosphate
Beryllium	Fluorine	Phosphorus
Cadmium	Formaldehyde	Pyrene
Chloride	HCl	Radium 226
Chlorine	HF	Selenium
Chromium	Lead	Toluene
Chromium–6	Manganese	Vanadium

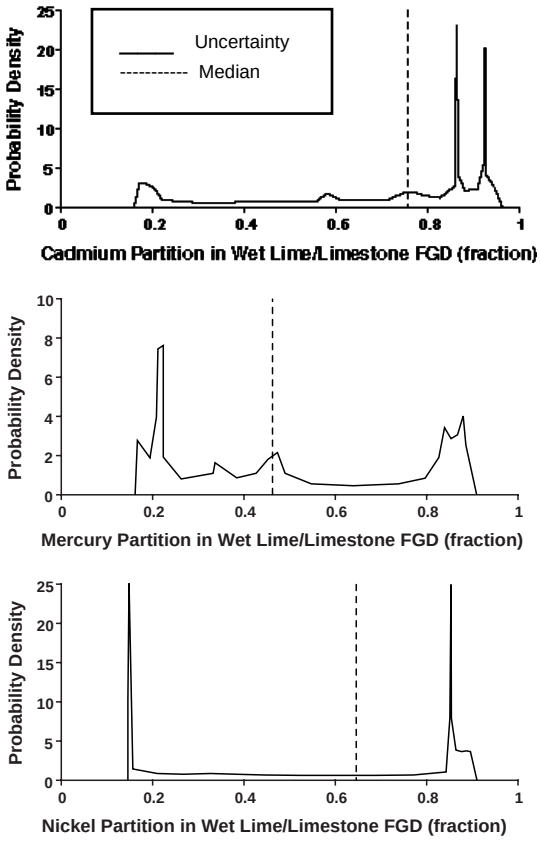

FIGURE 4. PARTITION FACTOR DATA SHOWING THE DISTRIBUTION OF TRACE SPECIES REMOVAL RATES IN LIME/LIMESTONE FGD SYSTEMS

recent years via more extensive testing. Figure 4 shows examples of partition factor data for three species (cadmium, mercury and nickel), indicating the fraction of each substance removed from the flue gas stream by wet lime or limestone FGD systems. These distributions represent 6 to 12 data points per species. The median value of each distribution is shown as a dashed vertical line. These values range from about 45 to 75 percent removal. However, there is substantial variability in these data, even for heavy metals such as cadmium. In the illustrative example that follows, these distributions are employed in the PISCES model along with other trace species and plant performance data to estimate the uncertainty in overall annual emissions from a typical power plant system.

MODEL APPLICATIONS

Applications to date of the PISCES Model have included, (1) deterministic studies of ten power plant configurations to benchmark key performance results against independent studies; (2) illustrative studies using early versions of the PISCES database; (3) comparisons of measured and predicted trace species flyash concentrations at a European power plant; (4) twelve utility–specific case studies carried out as part of the beta testing of the model; and (5) three case studies comparing model estimates with data from EPRI's field sampling program. Here we present some examples of results and insights obtained from use of the PISCES Model.

Mass Emission Estimates

Figure 5 shows illustrative examples of trace species mass emissions for a 300 MW power plant equipped with an electrostatic precipitator (ESP) and a wet scrubber. Here, the PISCES Model has been used together with the database partition factor distributions for the lime/limestone FGD systems shown earlier in Figure 4, plus similar distributions for tangentially-fired boilers and cold-side ESPs (see Figure 3). The results in Figure 5 show the relative magnitudes of total annual emissions for one of the six species modeled. The trace species coal concentrations used in this example are not for a single coal, but the distributions for all U.S. bituminous coals. Additional trace species enter in the FGD reagent.

Figure 5 decomposes the overall uncertainty into a number of constituent elements. The "spider plots" show the cumulative effect of adding uncertainties first in plant performance parameters (e.g., plant capacity factor), then additional variations in coal trace species concentrations, and finally the added uncertainties in the furnace, ESP and FGD partition factors. The final result yields a high degree of uncertainty in estimated emissions. In these examples, the effects of plant operating parameters are small compared to the trace species variability in coal. The added uncertainties in partitioning (removal efficiency) across the furnace, ESP and FGD system substantially extend the range of possible emissions from this plant, with the FGD partition factor uncertainty being dominant in this example.

Table 3 shows the relative values of the median, mean, and 90 percent confidence intervals of annual species emissions for this example. The 90 percent confidence interval for annual mercury emissions ranges by more than a factor of three hundred, while the range for cadmium is nearly 1000-fold. For a plant with one particular coal, the overall uncertainty would be much lower than the ranges shown here. Nonetheless, Table 3 shows that single-valued estimates do not adequately characterize the significant uncertainty that currently exists in estimating potential trace species emissions from coal-fired power plants.

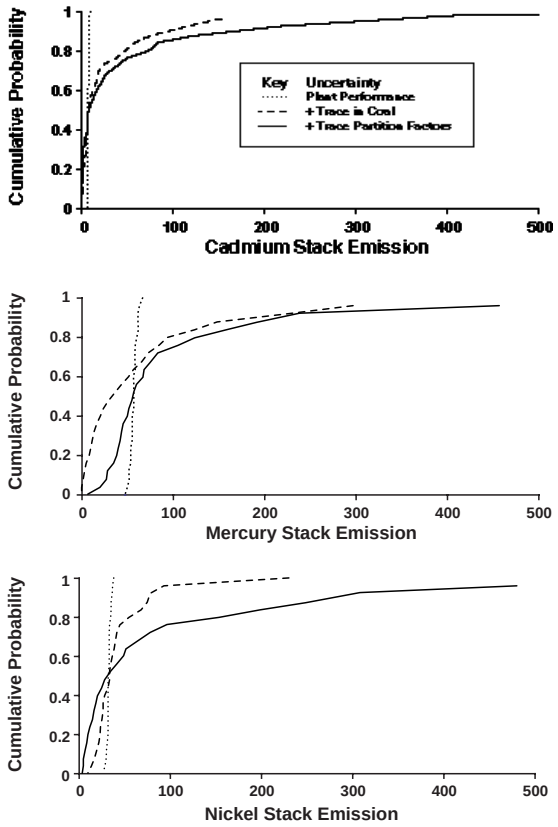

FIGURE 5. PROBABILISTIC RESULTS FOR ANNUAL TRACE SPECIES EMISSIONS BASED ON U.S. BITUMINOUS COALS

Comparisons of Measurements and Predictions

Figure 6 illustrates results from case studies using the PISCES Model and literature database to estimate emissions of trace elements from a coal-fired power plant equipped only with a cold-side ESP (Rubin, et al., 1993b). The distributions calculated by the PISCES Model are based on the actual site-specific coal properties and plant parameters, but use literature-based data for the furnace and ESP partitioning coefficients for units of similar design. For comparison, the reported error bars on the mean values of the site-specific measurements also are shown. This comparison indicates that while the mean values

TABLE 3. ANNUAL TRACE SPECIES EMISSIONS FOR ILLUSTRATIVE EXAMPLE (All Figures in Arbitrary Units)

Species	Median	Mean	90% CI[a]
Arsenic	113	338	8 - 1480
Cadmium	8	135	0.4 - 452
Chromium	17	43	0.6 - 168
Mercury	33	68	0.8 - 277
Nickel	29	100	4 - 376
Selenium	310	647	19 - 1930

[a] Confidence interval depicting the 5% and 95% probability values, respectively, from the uncertainty distribution, based on a sample size of 100 iterations.

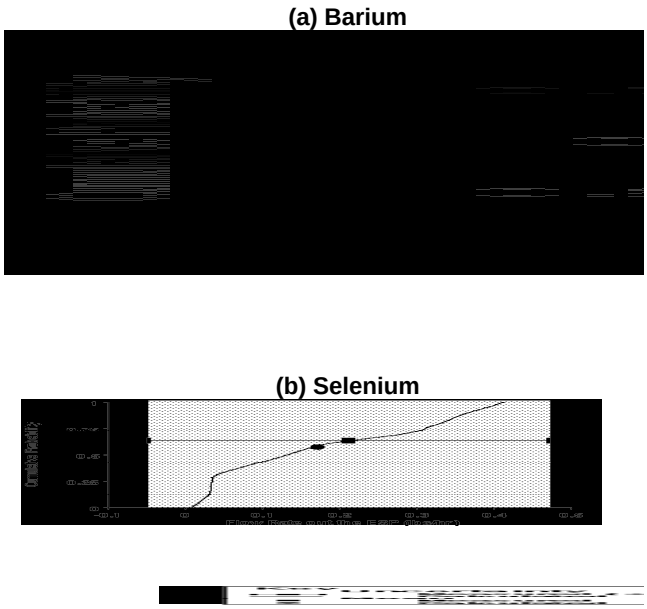

FIGURE 6. CALCULATED AND MEASURED TRACE SPECIES EMISSIONS AT A COAL-FIRED PLANT

of the predicted and measured mass emissions are similar for these cases, there remains significant uncertainty in both the reported site-specific experimental data and the predicted emission levels.

SOURCES OF UNCERTAINTY

We use the term "uncertainty" somewhat loosely to encompass all sources of variation in a given parameter of interest. More precisely, however, there are two often distinct sources of variation in the value of a quantity: uncertainty and variability. Uncertainty is the lack of knowledge about the true value of a quantity due to measurement error, systematic error, irreducible randomness, disagreement among experts, or lack of an empirical basis for making a prediction. In contrast, variability is the real fluctuation resulting from uncontrollable changes in the inputs to the system (Bogen and Spear, 1987; Morgan and Henrion, 1990; Taylor, 1993). These "noise" factors are manifested as a tangible variation in the system output that is irreducible without physical modifications to the system (i.e., study alone cannot reduce variability). Thus, even if we could measure trace species emissions with no uncertainty, we would still expect to see variation in emissions over time due to process variability.

For power plants, the primary sources of variability are changes in coal composition, changes in environmental control system performance, and other changes in process operating conditions that may influence the partitioning of trace species through the power plant over the course of the measurement period (which, for trace species, may be several days at any given facility). Furthermore, there may be variability between units in a larger population of plants of similar design.

Measurement error, on the other hand, has two components. One is random error, often referred to as lack of “precision.” The other is a systematic error or bias, often referred to as a lack of “accuracy.” Measurement errors may arise at all the steps involved in the measurement, including sampling at the site, sample preparation at the site and labs, and laboratory analyses. When measuring a matrix of trace species, interference between species can also induce measurement errors. Systematic error can arise from a tendency to consistently under- or over- recover certain species in the sampling trains, sample preparation, and analytical chemistry. There also may be systematic error between different laboratories.

Ongoing research efforts are seeking to refine knowledge of measurement error for individual trace species, and to develop more reliable methods for difficult-to-measure species such as mercury (Benson, et al., 1994). In the meanwhile, Bayesian statistical methods offer one means of obtaining better estimates of power plant trace species emissions by combining the measurement data with information from analytical modeling (Kalagnanam and Rubin, 1995). Future efforts to assess power plant air toxics can be expected to include more detailed characterizations of emissions uncertainty as part of on-going studies of risks and control options for hazardous air pollutants.

CONCLUSION

The power plant chemical assessment model developed as part of the EPRI PISCES program offers the capability to estimate multi-media hazardous substance emissions from a wide variety of electric power plant designs. The model's user–friendly graphical interface and ability to rigorously evaluate uncertainties make it a powerful analytical tool for general and site–specific studies of power plant effluents, risk assessments and emission control strategies. Future model developments will include enhanced capabilities for evaluating air toxics control options, as well as more detailed characterization of water-borne effluents needed to evaluate multi-media impacts.

ACKNOWLEDGMENTS

The work described here was supported by the Electric Power Research Institute under Research Project RP2933–2.

REFERENCES

Benson, S.A., et al., Eds., 1994, “Trace Element Transformations in Coal-Fired Systems,” *Fuels Processing Technology*, Vol. 39, Nos. 1-3, August.

Bogen, K.T. and R.C. Spear, 1987, "Integrating uncertainty and inter-individual variability in environmental risk assessment," *Risk Analysis*, Vol. 7, p. 427-436.

Kalagnanam, J.R., E. S., Rubin and M.B. Berkenpas, 1995, “Bayesian Methods for Reducing the Uncertainty in HAPs Emission Measurements,” *Proceedings of Third International Conference on Managing Hazardous and Particulate Air Pollutants*, Electric Power Research Institute, Palo Alto, CA, August.

Morgan, G.M. and M. Henrion, 1990, *Uncertainty*, Cambridge University Press.

Rubin, E.S. and M.B. Berkenpas,1993, "A Probabilistic Emissions Model for Managing Hazardous Air Pollutants," in *Managing Hazardous Air Pollutants: State of the Art*, W. Chow, and K.K. Connor, Eds., p. 329-348, Lewis Publishers.

Rubin, E.S., M.B. Berkenpas, H.C. Frey and B.T. O’Neil, 1993, “Modeling the Uncertainty in Hazardous Air Pollutant Emissions,” *Second International Conference on Managing Hazardous Air Pollutants*, Washington, DC, Electric Power Research Institute, Palo Alto, CA, July.

Rubin, E.S., J.R. Kalagnanam and M.B. Berkenpas, 1995, “New Models for FGD Performance, Cost and Hazardous Air Pollutant Removal,” *Proceedings of 1995 SO_2 Control Symposium, Electric Power Research Institute*, Palo Alto, CA, March.

Taylor, A.C., 1993, "Using objective and subjective information to develop distributions for probabilistic risk assessment," *J. of Exposure Analysis and Environmental Epidemiology*, Vol. 3(3), pp:285-298.

Wetherold, R.G., et al.,1995, “Structure, Content, and Use of PISCES Database,” *Proceedings of A&WMA 88th Annual Meeting and Exhibition*, Air and Waste Management Association, Pittsburgh, PA.