



Energy &
Environmental
Research
Center

Center for *Air Toxic Metals* Newsletter

May 1999

Volume 5 · Issue 1

Air Quality: Mercury, Trace Elements, and Particulate Matter

Experts from industry, government, environmental groups, and the research community met in McLean, Virginia, on December 1–4, 1998, for a four-day international conference on air quality.

The “Air Quality: Mercury, Trace Elements, and Particulate Matter” Conference was organized and sponsored by the Energy & Environmental Research Center (EERC), the U.S. Environmental Protection Agency (EPA) through the EERC’s Center for Air Toxic Metals (CATM), and the U.S. Department of Energy (DOE) Federal Energy Technology Center.

The conference provided up-to-date information on how human health and ecosystems can be impacted by hazardous air pollutants (HAPs) and fine airborne particles. Key issues covered included potential health risks, air pollution control technologies, research needs, and regulatory policies.

“There are important scientific questions related to the sources of these pollutants, their form and how they behave in the environment, our ability to accurately measure them, and the development of technologies to prevent and control them,” says Steve Benson, CATM Director. “The answers to these questions will directly affect state and national regulatory policies.”

Hg, which is toxic to humans, has been singled out for special study by EPA (see related articles on page 5 and in the Special Edition insert). Hg can remain in the atmosphere up to a year, be transported thousands of miles from its source, and does not degrade in the environment. Another pollutant affecting air quality is known as particulate matter, a mixture of solid and liquid particles suspended in the air. These particles degrade visibility and cause respiratory problems in humans. EPA is especially concerned about fine



U.S. Secretary of Energy Bill Richardson delivers keynote address in opening session.

particles known as PM_{2.5}. These microscopic particles are 2.5 microns or smaller (millions could fit on the head of a pin). Because they can be inhaled deeply into the lungs, PM_{2.5} can cause respiratory illnesses that lead to premature death. Children, the elderly, asthmatics, and people with heart and lung disease are especially susceptible to illnesses caused by fine-particle pollution (see related article in one-page Special Edition insert).

Richardson and Forrister Speak at Conference

U.S. Secretary of Energy Bill Richardson and White House Climate Change Task Force Chairman Dirk Forrister were among the 200 experts who participated in the Air Quality Conference.

Energy Secretary Richardson delivered a keynote address during the opening session of the conference entitled “Air Quality in the Future of Power Generation.” DOE is developing tech-

nology to monitor and control particulate matter. Much of the particulate matter in the atmosphere is produced by human activities, such as energy production and use, agriculture, wood stoves, and industrial processes.

“These unseen particles may pose respiratory problems for certain portions of the population, and for this Administration, there is no higher priority than protecting the health of our citizens,” says Richardson. “At the same time, if our clean air regulations are to be fair and scientifically sound, we need to understand much better the linkage between the levels of these pollutants in the atmosphere and their sources, both human and natural.”

Dirk Forrister, Chairman of the White House Task Force on Climate Change, delivered the banquet address. The Task Force, which is under the auspices of the President’s Council on Sustainable



White House Climate Change Task Force Chairman Dirk Forrister speaks at evening banquet.

Development, was created to advise the President on domestic policy options and activities that could reduce greenhouse

(continued on back page)



Steven A. Benson, Ph.D.

CATM in the Year 2000

Each year, CATM programs undergo review at the annual meeting of the Research Advisory Council (RAC), and directions for future research are identified. The RAC is made up of two committees, the Partners Advisory Committee (PAC) and the Science Advisory Committee (SAC). The role of the PAC is to identify research needs and ideas. The role of the SAC is to provide scientific review of proposals submitted. EERC scientists and engineers respond to the research needs with proposals that are reviewed by the SAC for scientific merit. The best proposals are selected for funding. This process ensures that practical, applied projects of high scientific merit are conducted.

The projects selected for the CATM program for the next year are summarized as follows.

■ **Fundamental Mechanisms of Mercury Species Formation in Power Plants**—Controlling and predicting Hg emissions from coal-fired power plants can be accomplished by improving the fundamental understanding of the mechanisms involved in Hg-flue gas-fly ash. The proposed research will discern and model the mechanisms by which $Hg^0(g)$ transforms to $Hg^{2+}X(s,g)$ and $Hg(p)$ in the postcombustion environment of a boiler because of interactions with flue gas components, especially $NO_2(g)$ and $SO_2(g)$.

■ **Reactive Sorbents for Cost-Effective Mercury Control**—Cost-effective Hg control for coal-fired boilers is a primary research need identified in the EPA Mercury Study Report to Congress. This project is intended to develop a test protocol and evaluate promising sorbents that are reactive enough to provide rapid in-duct Hg capture when injected upstream of a particulate control device. Based on past research, we now can hypothesize that interrupting or preventing one or more of the steps involving the interaction between SO_2 , NO_2 , and the sorbent surface will lead to improved Hg capture.

■ **The Stability of Mercury in**

Combustion By-Products—This project is designed to determine the stability and the levels of Hg released to the environment from coal or waste combustion by-products. Tests will be conducted to develop time and temperature profiles as a function of desorbed Hg. In addition, tests will be conducted to determine Hg offgassing at ambient or near-ambient temperatures and to determine the effects of light on Hg desorption.

■ **Application of Database and Models to the Fundamental and Applied Study of Air Toxic Metals**—The use of databases and models to predict and mitigate problems associated with air toxic metals has become a reality. Although actual testing is still necessary in most cases, databases and models can minimize the amount of testing needed by narrowing decisions, which allows both fundamental and applied research to be optimized. Data from the EPA Information Collection Request (ICR) will be added to the database when it becomes available. This project builds on the 6-year history of database, modeling, and research activities within the CATM program.

■ **Development of Sampling and Analytical Tools for Oxidized Mercury Species**—Bench-scale investigations of Hg sorbents in a gas stream containing Hg^0 and both NO_2 and SO_2 showed that breakthrough of Hg occurred in about an hour, compared with breakthrough times of several hours for the same sorbents in other gas mixtures. The Hg forms that were emitted from the sorbent into the gas stream were mainly oxidized species, but their identities are unknown. These interactions between Hg and gas components are also very important in understanding speciation of Hg in combustion flue gases and similar interactions that may occur on ash particles. Developing methods for determining the chemical composition and form of the volatile Hg species is critical to these goals.

■ **Mercury Release from Crude Oil**—This project will focus on gathering relevant information from a broad range of possible sources and evaluating the

information for accuracy, validity, and completeness. The information will be compiled into a final report that provides an assessment of the adequacy of available information and, assuming some information is available, the potential impact of Hg emissions from oil along with recommendations for addressing that impact.

■ **Investigation of the Fate of Mercury in Coal Combustion Plumes Using a Static Plume Dilution Chamber**—Measurements of the speciated forms of Hg can be made in the combustion stack as well as in ambient air. However, little is known about the Hg transformations that occur in the plume. Frontier Geosciences has developed a static plume dilution chamber (SPDC) to simulate plume conditions in the atmosphere and has shown positive results during tests in the field. Testing under more controlled conditions will be conducted using EERC's particulate test combustor to produce a flue gas of known composition that can be introduced into the SPDC.

■ **Fate of Fuel-Associated Inorganic Components in Combustion and Air Pollution Control Systems**—Technical information on the fate of fuel-associated inorganic components in combustion and air pollution control systems is voluminous. This project will present a workshop and a university course to provide attendees with up-to-date information on the effects of fuel-associated inorganic components on system performance and potential impact on the environment. Details of the course can be found on page 4 of the newsletter.

For more information, contact Steve Benson, CATM Director, at (701) 777-5177 or at sbenson@eerc.und.nodak.edu.

Technical Focus

Development of Catalytic Carbons for Mercury Sorption

The EPA *Mercury Study Report to Congress* identifies coal-burning utilities, medical waste incinerators, and municipal waste incinerators as the major contributors to anthropogenic mercury (Hg) emissions in the United States (1). Flue gas purification systems currently employed in these combustion sources are not adequate for control of total Hg emissions, owing to the high volatility at stack gas temperatures of 150°C or lower. Cost-effective options for treatment of the flue gas streams with Hg sorbents are needed. Current research in a Cooperative Agreement project with DOE and a CATM-funded project is directed toward achieving a better understanding of the types of sorbents that will be effective, the conditions under which different sorbents are effective, and the nature of the sorption mechanisms.

Treatment of a flue gas stream with powdered activated carbon is a developing technology for Hg removal. The carbon sorbent is injected into the flue gas upstream of a baghouse filter that collects the sorbent along with the ash. This method removed about 95% of

the Hg from an incinerator flue gas, which is likely to have been mostly HgCl_2 (2). The method also has great potential for elemental Hg (Hg^0), one of the major species present in coal combustion gas streams. Recent bench-scale studies indicate that the capacity for sorption of Hg on carbon is highly dependent on the conditions and presence of other flue gas constituents as well as Hg speciation (3). The present study into the development of Hg sorbent carbons seeks to identify factors that determine the kinetic reactivity of carbon sorbents for Hg^0 under controlled gas compositions.

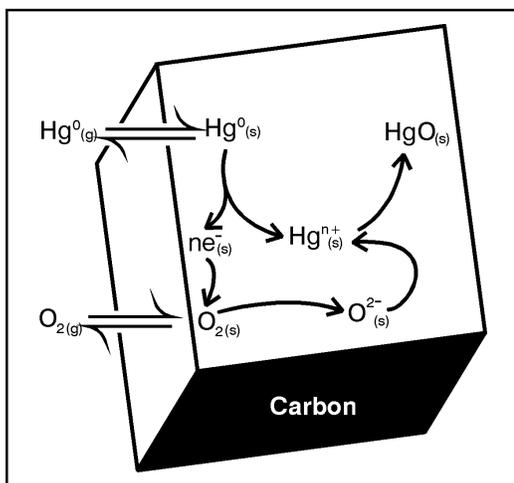
At temperatures above ambient, physisorption of Hg^0 on activated carbon was not expected to occur (4). In experiments performed with granular carbon sorbents (not impregnated) in air or in nitrogen streams at 23°C, breakthrough was almost instantaneous for carbon sorbents. The nonreactivity was apparent for slow as well as fast flow rates. Thus physisorption does not represent a significant mechanism for Hg^0 sorption, except at lower temperatures. In the presence of reactive gas components (such as O_2 , NO , NO_2 , or HCl), Hg sorption can occur at ambient conditions, owing to chemical reactions (oxidations) of the Hg^0 , and these may involve catalysis by the carbon sorbent.

Chemisorption rates are expected to increase with temperature. Experiments performed in an air stream with many of the carbon sorbents at progressively higher temperatures resulted in subsequently lower Hg concentrations in the effluent (higher Hg removal rates). In a nitrogen stream, however, there is no removal of Hg. Thus oxygen (O_2) must be utilized in the Hg chemisorption mechanism. Since different removal rates are exhibited by various carbon sorbents, the role of the carbon must be to catalyze the reaction of O_2 with Hg. Hall and coworkers describe the

catalysis of the reaction of Hg with O_2 at moderate temperatures by adding carbon (5).

Catalytic carbons are available that catalyze various aqueous reactions, such as decomposition of peroxides. The Calgon catalytic carbon (Centaur) is produced by re-carbonization of an ammonia-treated oxidized carbon. In studies performed in air at 150°C, the Hg^0 removal rate of the Centaur catalytic carbon exceeded that of other activated carbons. The higher kinetic activity persisted for a longer time, gradually decreasing to the 50% breakthrough point. A proprietary activation method was applied to the Centaur catalytic carbon prior to filling the sorbent tube (6). This increased the Hg^0 removal rate in air streams by a large factor. The activation method was substantially less effective in improving the removal rate for activated carbons that are not catalytic carbons. Therefore, the additive provides a promotion effect on the catalytic oxidation of Hg. Thus the combination of catalytic carbons and the activation method provides the key to effective Hg^0 sorption in air streams.

A large number of catalytic carbons were prepared at the EERC by a variety of methods (6), some of these for an earlier project in selective catalytic reduction (SCR) catalysis. The activities of the catalytic carbons were compared with the Centaur carbon for Hg^0 vapor sorption at 150°C in an air stream. Some of these exhibited very high Hg^0 removal rates. As with the Centaur carbon, the EERC carbons catalyzed the reaction of the Hg^0 with O_2 in the air stream. The removal rates at each temperature generally decreased slowly with time, exhibiting a gradual breakthrough. With many of the catalytic carbons, this occurred over several days, in most cases far surpassing the capacity of the Centaur carbon.



Elemental Mercury Sorption on Catalytic Carbon in Air

(Continued on page 5)

CATM Database Will Incorporate EPA ICR Data

The U.S. Environmental Protection Agency's (EPA) Information Collection Request (ICR), authorized under Section 114 of the Clean Air Act, requires coal-fired electric utility steam-generating units to provide information that will allow EPA to calculate the annual mercury (Hg) emissions from each unit. The information collected, along with additional input, will be used by EPA to determine whether future regulation of coal-fired electric utility units is necessary or appropriate.

The three-part ICR project follows the recommendations reported in EPA's *Final Report to Congress*, issued February 24, 1998, which studied hazardous air pollutants (HAPs) emitted from electric utility steam generating units and their potential risk to public health. The report found Hg to be the HAP of greatest potential concern and stated that additional research and monitoring were merited.

Part I of the ICR collected general information on all coal-fired electric utility steam generating facilities and was completed January 1999.

Part II, Coal Analyses Summary, currently under way, requires each facility to report the amount of coal received on a

per shipment basis for the calendar year. Hg and chlorine contents for each coal are also required for every sixth shipment of coal.

Part III, Speciated Hg Emissions Data, requires selected units first to submit a site-specific test plan and a Quality Assurance Project Plan (QAPP) to EPA for review and approval prior to testing, but no later than June 1, 1999. Following approval of the test plan and the QAPP, measurement of the abundance of Hg species in the flue gas is to be determined on a one-time basis at the inlet and outlet of the last pollution control device. All testing and emissions reports are to be provided to EPA no later than May 31, 2000.

Once the data are made available, they will be incorporated into the CATM database, which is a powerful tool with the capability to analyze the ICR data in terms of mass balances, combustion efficiencies, and emissions. In addition to serving as an unbiased data source, the CATM database will allow researchers, industry, and regulators to perform necessary calculations, comparisons, and correlations with the data. The database can also be used to compare and contrast the effects of coal type, combustion sys-

tems, and environmental control systems on the emission of Hg. Additionally, collection efficiencies and mass balances can be performed around collection devices. The mass balances, along with data quality flags and analytical information, can aid the user in identifying suspect data.

The CATM database currently contains information from full- and pilot-scale units firing coal and has been designed as a powerful tool to aid researchers, regulators, and industry. In addition to serving as a detailed source of engineering, analytical, and material information, the database also allows the user to perform 1) data quality checks, 2) mass balances, 3) collection efficiencies, 4) emission predictions, and 5) data correlations and comparisons. The CATM database can be accessed through www.eerc.und.nodak.edu/catm/database.html.

For more information, please contact John Pavlish, CATM Associate Director, at (701) 777-5268 or at jpavlish@eerc.und.nodak.edu. For information related to the CATM database, please contact Tom Erickson, EERC Senior Research Manager, at (701) 777-5153 or at terickson@eerc.und.nodak.edu.

Course to Be Made Available on Internet and CD-ROM

"Fate of Fuel-Associated Inorganic Components in Combustion and Air Pollution Control Systems"

Fuel-associated inorganic components have major impacts on the performance of combustion systems and can have environmental implications if not captured in control devices or disposed of properly. Technical information on the fate of fuel-associated inorganic components in combustion and air pollution control systems is voluminous. The EERC is aware of such work and for the past 50 years has performed research, development, and demonstration programs that have developed highly efficient power and associated air pollution control systems. The EERC, through its CATM program, will develop and present a course to consolidate pertinent information gleaned from the 5000-plus journals, conference proceedings, and government reports on this subject.

A course entitled "Fate of Fuel-Associated Inorganic Components in Combustion and Air

Pollution Control Systems" will be offered as a three-credit course through the Chemical Engineering Department to students at the University of North Dakota, other universities, government agencies, and industry in January 2000. The course aims to inform participants on the current state of understanding of major, minor, and trace inorganic components in combustion and conversion systems. This will aid developers of technologies to make more informed decisions on system design, give researchers in-depth background information as a basis for their work, and provide educators/students with detailed information for research and instruction.

The audio and slides presented during the lectures will also be made available to students over the Internet. An enhancement will be made to the EERC Web site to include all course materials and each class.

The course outline will consist of 1) Intro-

duction, 2) Inorganic Constituents in Fuels, 3) Methods of Determining Inorganic Components in Fuels, 4) Description of Combustion and Environmental Control Systems and Associated Performance and Environmental Problems, 5) Mechanisms of Inorganic Transformations in Combustion/Gasification and Environmental Control Systems, 6) Combustion and Gasification Process Impacts – Fireside Slag Flow and Ash Deposition, 7) Air Pollution Control Devices, 8) Modeling the Behavior of Inorganic Components, 9) Fate in the Ecosystem, 10) Health Impacts, and 11) Future Directions for Power and Control Systems.

If you would like to sign up for this class, please contact Steve Benson, CATM Director, EERC, at (701) 777-5177 or at sbenson@eerc.und.nodak.edu.

The Ontario Hydro Mercury Speciation Sampling Method

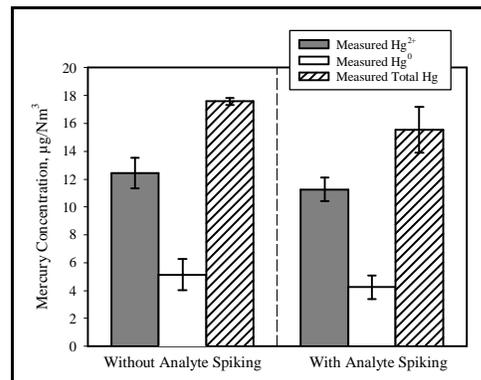
The 1990 Clean Air Act Amendments (CAAA) required EPA to determine the forms (species) and abundance of Hg in the stack emissions from fossil fuel-fired electric utility power plants. This information will be used to determine if there is an unacceptable public health risk. Given the current state of understanding, it is not known if Hg controls on coal-fired electric power stations are required. However, based on the *Mercury Study Report to Congress*, it was clear that the EPA viewed Hg as a potential threat to human health. Therefore, EPA indicated that additional research and information were necessary before a definitive statement on Hg controls on power plants could be made. Consequently, in the fall of 1998, EPA issued an Information Collection Request (ICR). Approximately 80 power plants, based on plant configuration and coal type, were selected for sampling and analyses of Hg. The flue gas Hg sampling method required for the ICR is the Ontario Hydro (OH) Hg speciation method.

The OH method was first proposed by Dr. Keith Curtis of Ontario Hydro. The method was further developed, tested, and validated at the EERC. In August 1998, a validation test of the method was completed at a midwestern power plant burning a medium- to high-sulfur coal. As seen in the figure, the error bars indicate

good precision (each error bar represents 20 data points). Based on these results, the method easily passed the 50% relative standard deviation criteria (there was no statistical bias) established in the EPA Method 301 method validation procedure.

The OH method is currently being evaluated by the D22.03 subcommittee of the ASTM. It is expected that in October 1999 a full ballot will be taken and the method will be accepted by the ASTM. The method is currently posted on the EPA TTN web page at <http://www.epa.gov/ttn/emc/prelim.html> under "PRE 3." The most recent version is dated April 8, 1999.

After performing the OH method more than 500 times at power plants and test facilities, EERC researchers have found that the OH method is complicated, and extreme attention to detail is absolutely necessary. Personnel using this method must have experience in flue gas sampling methods. In addition, quality control/quality assurance is absolutely critical when using the method. Hg is typically present in the flue gas in a range of 5 to 20 $\mu\text{g}/\text{Nm}^3$. At these concentrations, erroneous results are possible unless great care is taken during all aspects of the procedure. Also, especially for the ICR testing, it is highly recommended that an external QA/QC evaluation of the



Reproducibility of the OH Hg Speciation Sampling Method

sampling team and analytical laboratories be done. This external evaluation is not meant to be regarded as an audit but rather to ensure that proper procedures are used. EPRI is providing a statement for sampling with the OH method for the ICR, "Key Points for Conducting Mercury Speciation Stack Sampling." To obtain a copy of this document, please e-mail Paul Chu at pchu@epri.com.

For additional information, please contact Dennis Laudal, EERC Research Manager, at dlaudal@eerc.und.nodak.edu or at (701) 777-5138.

(Catalytic Carbons, continued from page 3)

Subsequent work showed that the composition of the gas phase is critically important in determining the ability of any carbon sorbent to chemisorb Hg^0 at these temperatures. A series of bench-scale tests were performed in reactive flue gases to determine the removal rates of carbon sorbents at moderate temperatures under combustion conditions (3). These investigations included studies with flue gas component gases to determine their effects on Hg oxidation on the sorbent surface. The baseline flue gas composition included O_2 (6%), CO_2 (12%), SO_2 (1600 ppm), HCl (50 ppm), Hg^0 (20 $\mu\text{g}/\text{m}^3$), H_2O (8%), and N_2 (balance). Later, studies were performed with NO_x species added to the gas stream.

The results of tests in the baseline gas composition indicated that there was little difference between the catalytic carbons

and other carbons in the acidic gas atmospheres. This contrasts significantly from the results of the tests conducted in air streams. Thus other effects such as the $\text{Hg}-\text{HCl}$ reaction (7) dominate the sorption chemistry occurring on the carbon. A report on the results in the acidic gas streams will follow in a subsequent issue of the *CATM Newsletter*.

References

- 1 U.S. Environmental Protection Agency. *Mercury Study Report to Congress*; EPA-452/R-97-101, Dec 1997.
- 2 Liberti, L.; Notarnicola, M.; Amicarelli, V.; Campanoro, V.; Roethel, F.; Swanson, L. *Waste Manage. Res.* **1998**, *16*, 183.
- 3 Miller, S.J.; Olson, E.S.; Dunham, G.E.; Sharma, R.K. Preparation Methods and Test Protocol for Mercury Sorbents. Presented at Air & Waste Management Association 91st Annual Meeting, San Diego, CA, June 14, 1998.
- 4 Sinha, R.K.; Walker, P.L. *Carbon* **1972**, *10*,

754.

- 5 Hall, B.; Schager, P.; Lindquist, O. *Water, Air, Soil Pollut.* **1991**, *56*, 3.
- 6 Olson, E.S. U.S. Patent application, submitted Aug 1997.
- 7 Young, B.C.; Musich, M.A. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1995**, *40*, 833.
- 8 Nguyen, X.T. *J. Air Pollut. Control Assoc.* **1979**, *29*, 235.

For more information, please contact Ed Olson, EERC Senior Research Advisor, at (701) 777-5155 or at eolson@eerc.und.nodak.edu; or Stan Miller, EERC Senior Research Manager, at (701) 777-5210 or at smiller@eerc.und.nodak.edu.

inside. . .

- **Air Quality: Mercury, Trace Elements, and Particulate Matter**
- **Director's Message: CATM in the Year 2000**
- **Technical Focus: Development of Catalytic Carbons for Mercury Sorption**
- **CATM Database Will Incorporate EPA ICR Data**
- **The Ontario Hydro Mercury Speciation Sampling Method**

(Air Quality, continued from front page)

gas emissions using approaches that maximize societal benefits, minimize economic impacts, and are consistent with U.S. international agreements.

U.S. Senator Kent Conrad (D, ND) also delivered a keynote address in the opening session entitled "Making Public Policy in the Face of Uncertainty: The Need for Solvent Scientific Information." U.S. Senator Byron Dorgan (D, ND) gave a luncheon address, "Current Issues in Air Quality."

Rita Bajura, Director of the DOE Federal Energy Technology Center, and Peter Preuss, Director of the EPA's National Center for Environmental Research and Quality Assurance in the



U.S. Senator Kent Conrad delivers keynote address

Office of Research and Development, provided opening comments, along with Steve Benson, CATM Director, and Gerald Groenewold, EERC Director.

An evening poster session sponsored by Northern States Power Company offered conference participants 28 posters to further discussion on the many issues surrounding the all-encompassing topic of air quality.

Two panel discussions rounded out the conference, with leading experts representing health and environmental sciences making up the panel on "Air Quality Science and Technology" and key



U.S. Senator Byron Dorgan delivers luncheon address

representatives of U.S. Congressional committees, federal and state agencies, environmental advocacy groups, and industry leading discussions on the "Environmental Policy" panel.

For more information, please contact Steve Benson, CATM Director, at (701) 777-5177 or at sbenson@eerc.und.nodak.edu, or John Pavlish, CATM Associate Director, at (701) 777-5268 or at jpavlish@eerc.und.nodak.edu.

Acknowledgments

This newsletter is funded wholly or in part by the U.S. Environmental Protection Agency through its Office of Research and Development under assistance agreements CR821518, CR823173, and R824854. It has not been subjected to EPA review and therefore does not necessarily reflect the views of the EPA, and no official endorsement should be inferred.

Constance Wixio, Editor

Phone: (701) 777-5161 Fax: (701) 777-5181
E-mail: cwixio@eerc.und.nodak.edu
We welcome your comments.