# Final Progress Report

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**Project Title**: Measurements and Control of Diesel Emissions in Underground Mines

**Grant #**: R01 OH007679

**Co-Investigators**: Dr. Tim C. Keener
Dr. Soon-Jai Khang

**Sponsor**: National Institute of Occupational Safety and Health

**Project Start Date**: September 1, 2002

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## List of Abbreviations

DPM: diesel particulate matter
CESP: condensation electrostatic precipitators
NIOSH: National Institute for Occupational Safety and Health
IARC: International Agency for Research on Cancer
WHO: World Health Organization
EPA: California Environmental Protection Agency
OC: organic carbon
EC: elemental carbon
PAH: polycyclic aromatic hydrocarbons
DPF: diesel particulate filters
PASH: polycyclic aromatic sulfur heterocycles
GC/MS: gas chromatography and mass spectroscopy
TMBTs : trimethylbenzothiophenes
DBTs: dibenzothiophenes
4-MDBT: 4-methyldibenzothiophene
IC: Ion Chromatography
XRF: X-Ray Fluorescence
ELPI: electrical low pressure impactor
HC: hydrocarbon

## Abstract

This project addresses the health and safety concerns of underground mine workers with respect to diesel particulate matter (DPM) exposure. The underground mine workers have higher DPM exposures due to the enclosed environment and the many diesel equipment used underground. DPM has been designated as carcinogenic and or mutagenic by various agencies including the National Institute for Occupational Safety and Health (NIOSH), the International Agency for Research on Cancer (IARC), the World Health Organization (WHO), the California Environmental Protection Agency (EPA), the U.S. EPA, and the National Toxicology Program. Comparing with on road diesel machines, the non-road ones are much less studied due to less visibility and more varieties. Therefore, it is essential to quantify the DPM composition in terms of OC (organic carbon), EC (elemental carbon) and PAH (polycyclic aromatic hydrocarbons) compounds from diesel fuel, engine oil and DPM. In this project, a nonroad diesel generator operating at varying load conditions was used as a stationary diesel emission source. The development of a condensation electrostatic precipitator (CESP) is to provide more effective DPM control without causing high back pressure as would the diesel particulate filters (DPF). This research revealed strong effects from engine operation conditions and sampling methods on the organic composition and formation mechanisms of DPM, as well as the compound distribution. Lower sampler temperature results in more DPM mass and higher concentrations of organic species. Higher engine loads caused the increase in DPM emission rate, its elemental carbon fraction, and the heavier components, which were formed during combustion processes, and may present greater health risks. The OC fraction, on the other hand, is higher at lower engine load. Results showed that, $SO_2$ concentration increases as diesel sulfur content or engine load increases, similar to that of DPM. In this study, experiments were performed with a bench-scale tube-type wet electrostatic precipitator (wESP) and its effectiveness for the removal of mass- and number-based diesel particulate matter (DPM), hydrocarbons (HCs), CO, and NOx from diesel exhaust emissions was evaluated. The DPM mass was determined by a gravimetric method and the number concentration was quantified by an electrical low pressure impactor (ELPI). The wESP was capable of removing ~67% to ~86% of mass- and number-based DPM at a 100% exhaust volumetric flowrate from 0- to 75-kW engine loads. The removal of organic compounds and CO in the wESP ranged from 31%-57%, and 5%-38%, respectively. The wESP (wet ESP) was evaluated with respect to different operational control parameters such as applied voltage, gas residence time, etc., to determine their effect on overall collection efficiency, as well as particle size dependent collection efficiency. The increase of exhaust gas residence time within the wESP from 0.1 to 0.4 s led to a substantial increase in the collection efficiency from 67% to 96%. The collection efficiency was found to increase with increases in applied voltage.

## Highlights/Significant Findings

- DPM emission is proportionally related to the fuel sulfur content and the engine load, and increase with these two parameters.
- The fractions of OC decreases with load while EC increases with load. The sulfur content in diesel fuel contributes to higher fractions of OC and non-carbonaceous materials of the DPM emissions than the low sulfur diesel fuel. At lower DPM collection temperatures, more OC and non-carbonaceous materials are observed.
- In the study of organic sulfur speciation, trimethylbenzothiophenes (TMBTs), dibenzothiophenes (DBTs), and 4-methyldibenzothiophene (4-MDBT) were the most abundant sulfur compounds in diesel fuel. The high-sulfur diesel fuel contained a larger proportion of PASHs with one or two rings (lighter PASHs). In DPM, the concentrations of total organic sulfur and individual PASHs are higher for the high-sulfur diesel fuel, and the relative percentage of one or two-ring PASHs is higher as well. The influence of engine load on the DPM composition was also examined. With increasing load, the PASH concentration in DPM decreased for lighter PASHs, increased for heavier PASHs, and had a bell-shaped distribution for PASHs in between, as an indication of whether they are pyrogenic (formed from combustion) or petrogenic (exist in the fuel).
- The wESP (wet ESP) was evaluated with respect to different operational control parameters such as applied voltage, gas residence time, etc., to determine their effect on overall collection efficiency, as well as particle size dependent collection efficiency. The increase of exhaust gas residence time within the wESP from 0.1 to 0.4 s led to a substantial increase in the collection efficiency from 67% to 96%. The collection efficiency was found to increase with increases in applied voltage. The measured collection efficiency of the wESP operating at 70 kV based on total particle numbers was 86% at 0 kW engine load and the efficiency decreased to 67% at 75 kW due to a decrease in gas residence time and an increase in particle concentrations. The collection efficiency based on particle size had a minimum for sizes between 20 and 50 nm, but at optimal wESP operating conditions it was possible to remove over 90% of all particle sizes.
- The wESP was capable of removing ~67% to ~86% of mass- and number-based DPM at a 100% exhaust volumetric flowrate from 0- to 75-kW engine loads. The removal of organic compounds and CO in the wESP ranged from 31%-57%, and 5%-38%, respectively.
- The sulfur speciation results showed that, $SO_2$ concentration increases as diesel sulfur content or engine load increases, similar to that of DPM.

## Translation of Findings

The prototype CESP developed from this project can be installed onto the diesel machines in the underground mines to protect the health of the mineworkers, and can reduce the emissions of both gaseous and particulate diesel emissions. This technology can be an alternative to the diesel particulate filters. The CESP can be potentially more advantageous to the DPFs for older diesel machines. The load variated compositional studies on diesel fuel, DPM and engine oil, on the other hand, can provide more accurate information on what pollutants to protect against, as the DPM emissions vary with the load (working) conditions. It can also provide more guidance on the regulations regarding non-road DPM emissions.

## Outcomes/Relevance/Impact

The project has resulted in the development of a CESP which can be applied to underground mines to control DPM emissions. Although it is a prototype ESP, it can reduce the emissions of both gaseous and particulate diesel emissions. The DPM compositional study has provided better understanding of the sampling artifact of the high-volume DPM sampler, and quantified the load varied DPM emissions in terms of OC, EC and PAHs. The measurements also suggested that the DPM emission is related to the properties of the fuel, the engine oil, and the combustion conditions, and most of the heavy PAHs are combustion generated (pyrogenic). The compositional study of the PASH (polycyclic aromatic sulfur heterocycles) compounds in diesel fuel and DPM will result in a NIOSH test method in the future to quantify the sulfur containing compounds.

This project has also resulted in the close collaboration with two NIOSH research facilities. The collaboration with the NIOSH Research Laboratory in Cincinnati, OH focuses on DPM compositional characterization, has used NIOSH facilities such as the OC/EC analyzer, and the GC/AED (gas chromatography/atomic emission detector), and has resulted in two journal articles published (1 or 2 more expected). The prototype CESP will be tested by the NIOSH Research Laboratory in Pittsburgh, PA at their Laky Lynn facility to evaluate its effectiveness in DPM control. It is expected that some highly valuable recommendations will be made to better improve the ESP design with the expertise from this NIOSH group.

The project has resulted in two PhD dissertations and one MS thesis. Mr. Zifei Liu has received the Pat Scarpino Award for best MS thesis from the Univ. of Cincinnati in 2005, under the sponsorship of this project. The project has resulted in 5 papers in peer reviewed journals, 5 peer –reviewed conference proceedings and 16 conference presentations and posters (including the ones with proceedings).

## Scientific Report

**Background:** Studies have indicated that diesel exposure in underground mines is much higher than the other occupational exposures, such as truck drivers, forklift workers and fire fighters. Although further characterization of organic speciation of DPM emissions is still on-going, the hazardous effects of DPM emissions has been confirmed by various agencies, including the National Institute for Occupational Safety and Health (NIOSH), the International Agency for Research on Cancer (IARC), the World Health Organization (WHO), the California Environmental Protection Agency (EPA), the U.S. EPA, and the National Toxicology Program. There have been limited studies on the organic compositions due to the complexity of the DPM matrix, as well as sampling and instrumentation limitations. Post combustion control techniques which have been applied to diesel exhaust include oxidation catalytic converters, disposable diesel exhaust filters, and ceramic particulate filters. Problems with these systems exist, however. Oxidation catalytic converters may not be able to provide the level of control efficiency required to protect miners' health. Disposable filters must be changed frequently due to ash (soot) build-up and the subsequent increase in pressure drop (engine back pressure), which affects engine performance. Ceramic filters must have a regeneration step at high temperature, which means that either two units must be used for continuous operation (one in filtration mode and one in regeneration mode), or the filter must be taken off-line to be regenerated.

Despite the progress in DPM knowledge in underground mines, there are still gaps to fill, especially in the areas of organic speciation in both gaseous and particulate phases. Innovation in DPM control technology is essential to the improvement over current end-of-pipe technologies in order to achieve higher efficiency, and easier operation and maintenance.

**Specific Aims:** The overall goal of this project is to accurately characterize particulate diesel emissions in underground mines and to develop an effective source control technology for diesel emission reduction. The specific aims are two folds. The aim of DPM (diesel particulate matter) characterization is to quantify the organic compositions (such as polycylic aromatic hydrocarbons, nitro-compounds and oxygenated compounds etc.), DPM personal exposure level, and to evaluate the effectiveness of the proposed control technology, in order to provide more accuracy in addressing health risks associated with DPM exposure. The aim of the CESP (condensation electrostatic precipitator) design is to develop an effective control technology that is more efficient in terms of DPM, gas and vapor control, as well as cost effective and safe for underground mines.

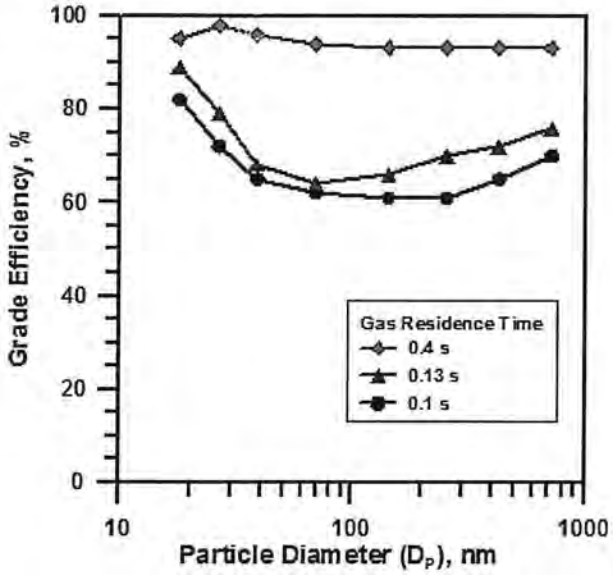
**Methodology:** A non-road diesel generator was used in this study for DPM measurement and control. The #2 diesel fuel was used, with fuel sulfur contents ranging from 3700 ppm to 500ppm. The exhaust pipe of the generator was extended for sampling purposes. For DPM compositional study, a high-volume sampler (up to 300 liters per minute) was developed with a dilution system. A load simulator was installed to simulate various load conditions from idle to full load. EPA Method 5 (Determination of

Particulate Matter Emissions from Stationary Sources) was performed to evaluate the OC/EC distribution vs. load, the fuel sulfur content variation with DPM emissions, and the control efficiency of the CESP. EPA Method 8 (Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources) was used to measure the sulfur containing species (SO2 and sulfate) in diesel emissions. The organic composition was measured by the dilution system and the analysis was conducted on GC/MS (gas chromatography and mass spectroscopy). GC/AED was used to analyze the individual PASH compounds. Particulate sulfate ($SO4^{2-}$) and total particulate sulfur in DPM were determined by Ion Chromatography (IC) and X-Ray Fluorescence (XRF) spectroscopy analysis respectively.

A tubular wet ESP was developed with a cooling system to cool down the exhaust gas. The wESP (wet ESP) was evaluated with respect to different operational control parameters such as applied voltage, gas residence time, etc., to determine their effect on overall collection efficiency, as well as particle size dependent collection efficiency. The hydrocarbon (HC) compounds (*n*-alkanes and PAHs) were collected on a moisture-free quartz filter together with a PUF/XAD/PUF cartridge and extracted in dichloromethane with sonication and analyzed with GC/MS. A calibrated gas combustion analyzer (Testo 350) was used for quantifying the inlet and outlet concentrations of CO and NOx (NO+NO2), respectively.

**Results and Discussion:** Our studies have indicated that the DPM emissions increase with both the load and the fuel sulfur content. An empirical correlation for estimating DPM concentration is obtained: $Y = Z^m(\alpha X + \beta)$, where Y is the DPM concentration, $mg/m^3$, Z is the fuel sulfur content, $ppm_w$ (limited to 500-3700 $ppm_w$), X is the applied load, kW, m is the constant, 0.407, $\alpha$ and $\beta$ are the numerical coefficients, 0.0118 and 0.4535, respectively. More than 80% of DPM is carbonaceous material. The fractions of OC decreases with load while EC increases with load. Both the organic compounds and non-carbonaceous materials contribute more to DPM in the high sulfur diesel emissions than in the low sulfur diesel emissions. At lower collection temperatures, more OC and non-carbonaceous materials are observed. In the study of organic sulfur speciation, trimethylbenzothiophenes (TMBTs), dibenzothiophenes (DBTs), and 4-methyldibenzothiophene (4-MDBT) were the most abundant sulfur compounds in diesel fuel. The high-sulfur diesel fuel contained a larger proportion of PASHs with one or two rings (lighter PASHs). In DPM, the concentrations of total organic sulfur and individual PASHs are higher for the high-sulfur diesel fuel, and the relative percentage of one or two-ring PASHs is higher as well. The influence of engine load on the DPM composition was also examined. With increasing load, the PASH concentration in DPM decreased for lighter PASHs, increased for heavier PASHs, and had a bell-shaped distribution for PASHs in between, as an indication of whether they are pyrogenic (formed from combustion) or petrogenic (exist in the fuel). Results showed that, SO2 concentration increases as diesel sulfur content or engine load increases, similar to that of DPM. The sampling artifact of the sampling methods, EPA Method 5 and the high-vol. method, have been evaluated and corrected.

The results show that the total DPM number concentrations in the untreated diesel exhaust are in the magnitude of 10 $^{8}$/cm3 at all engine loads with the particle diameter modes between 20 and 40 nm. The measured collection efficiency of the wESP operating at 70 kV based on total particle numbers was 86% at 0 kW engine load and the efficiency decreased to 67% at 75 kW due to a decrease in gas residence time and an increase in particle concentrations. At a constant wESP voltage of 70 kV and at 75 kW engine load, the variation of gas residence time within the wESP from 0.1 to 0.4 s led to a substantial increase in the collection efficiency from 67% to 96%. The collection efficiency was found to increase with increases in applied voltage. The collection efficiency based on particle size had a minimum for sizes between 20 and 50 nm, but at optimal wESP operating conditions it was possible to remove over 90% of all particle sizes. The wESP was capable of removing ~67% to ~86% of mass- and number-based DPM at a 100% exhaust volumetric flowrate from 0- to 75-kW engine loads. The removal of organic compounds and CO in the wESP ranged from 31%-57%, and 5%-38%, respectively.




**Conclusions:** This project has demonstrated the effectiveness of the wESP to control DPM emissions, which can be potentially developed as an alternative DPM control technology in addition to the DPFs. The methods for sampling and analysis of DPM have been developed to characterize the fuel, engine oil and DPM emissions, as well as to evaluate the effectiveness of the control technology. The removal efficiency is evaluated by various methods, including the traditionally mass based, the number based, and on the chemical composition basis. More testing (in laboratory or in the field) of the wESP is recommended to develop this technology into a full fledged commercial product for the protection of DPM emissions.

## Publications

The project has resulted in 5 papers in peer reviewed journals, 5 peer –reviewed conference proceedings and 16 conference presentations and posters (including the ones with proceedings).

Journal publications related to the specific aim of characterization of DPM emissions

- F. Liang, M. Lu, M. E. Birch, T. Keener, and Z. Liu: [2006] "Determination of Polycyclic Aromatic Sulfur Heterocycles in Diesel Particulate Matter and Diesel Fuel by Gas Chromatography with Atomic Emission Detection", *J. Chromatography A,* 1114 (1): 145-153.
- Z. Liu, M. Lu, T. Keener, E. Birch, S. Khang, F. Liang: [2005] "Variations of the particulate carbon distribution for a nonroad diesel generator", *Environmental Science and Technology*, 39: 7840-7844.
- F. Liang, M. Lu, T C. Keener and Z. Liu: [2005] "The organic composition of diesel particulate matter, diesel fuel, and engine oil of a non-road diesel generator", *Journal of Environmental Monitoring,* 7: 983-988.

Journal publications related to the specific aim of development of control technology

- P. Saiyasitpanich, M. Lu T.C. Keener, S-J. K., F. Liang: [2005] The effect of diesel fuel sulfur content on particulate matter emissions for a nonroad diesel generator, J. Air & Waste Manage. Assoc., 55, 993-998.
- P. Saiyasitpanich, T.C. Keener, M. Lu, S-J. K., D.E. Evans: [2006] Collection of ultrafine diesel particulate matter (DPM) in cylindrical single-stage wet electrostatic precipitators, Environ. Sci. Technol. *40*(24), 7890 – 7895.

Conference posters/presentations related to the specific aim of characterization of DPM emissions

- F. Liang and M. Lu:[2006] "Phase Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Diesel Emissions from A Non-road Generator", the annual AAAR (American Association for Aerosol Research) Conference, Sept. 10-15, 2006, St. Paul, MN.
- Fuyan Liang, Mingming Lu, Tim. C. Keener, Zifei Liu: [2006] "The Effect Of Dilution On Organic Composition Of Diesel Particulate Matter", 16th CRC On-Road Vehicle Emissions Workshop, March 28-30, 2006, San Diego, California.
- Zifei Liu, Mingming Lu, Tim. Keener, Fuyan Liang :[2005], "The effects of dilution process on the distribution of OC, EC and sulfate in diesel particulate matter (DPM)", the annual AAAR (American Association for Aerosol Research) Conference, Oct. 16-20, 2005, Dallas, TX.
- Zifei Liu, Mingming Lu, Tim C. Keener, Soon-Jai Khang and Fuyan Liang, :[2005] "The sulfur speciation of diesel emissions from a non-road generator", presentation, the 98th A&WMA Annual Conference and Exhibition; June 21-24, 2005, Minneapolis, MN.

- Fuyan Liang, Mingming Lu, Eileen Birch, Tim C. Keener, Soon-Jai Khang and Zifei Liu :[2005] "the effect of diesel fuel sulfur content on the organic speciation of diesel particulate matter", presentation, the 98th A&WMA Annual Conference and Exhibition; June 21-24, 2005, Minneapolis, MN.
- Mingming Lu, Fuyan Liang, Tim C. Keener, Soon-Jai Khang and Zifei Liu :[2004] "The organic compositions of diesel fuel, engine oil, and diesel particulate matter from a non-road diesel engine", presentation, the 2004 Ohio Air quality conference, Dec. 2-3, 2004, Athens, OH.
- Zifei Liu, Mingming Lu, Tim C. Keener, Soon-Jai Khang :[2004] "The sampling artifacts of a high-vol. sampling system", the AAAR (American Association for Aerosol Research) 2004 Conference, Oct. 4-8, 2004, Atlanta, GA.
- Fuyan Liang, Mingming Lu, Tim C. Keener, Soon-Jai Khang and Zifei Liu:[2004] "The effect of load on organic species in diesel particulate matter (DPM)", the AAAR (American Association for Aerosol Research) 2004 Conference, Oct. 4-8, 2004, Atlanta, GA.
- M. Lu, T. Keener, E. Birch, S. Khang, F. Liang, Z. Liu:[2004] "The OC/EC distribution of non-road diesel machines under various loads", proceedings of the 97th A&WMA Annual Conference and Exhibition; June 22-25, 2004, Indianapolis, IN
- Fuyan Liang, Mingming Lu, Tim Keener, and Zifei Liu:[2004] "The composition analysis of diesel fuel and diesel emissions with GC/MS", proceedings of the 97th A&WMA Annual Conference and Exhibition; June 22-25, 2004, Indianapolis, IN
- Fuyan Liang and Mingming Lu:[2004] "The composition analysis of diesel fuel and diesel emissions with GC/MS", student poster forum of the Univ. of Cincinnati, March 12 2004, Cincinnati, OH.
- Fuyan Liang, Mingming Lu, Tim C. Keener and Zifei Liu:[2003] "The PAC compounds in diesel fuel and DPM", poster, the 2003 Ohio Air quality conference, Oct. 29, 2003, Toledo, OH.
- Mingming Lu, Tim C. Keener, Eileen M. Birch, Soon-Jai Khang, Zifei Liu and Fuyan Liang:[2003] "The OC/EC Distribution vs. Load of Non-road Diesel Machines", presentation, the 2003 Ohio Air quality conference, Oct. 29, 2003, Toledo, OH.

<u>Conference posters/presentations related to the specific aim of development of control technology</u>

- P. Saiyasitpanich, T.C. Keener: [2006] Control of diesel particulate emissions using a wet electrostatic precipitator, Graduate poster forum, University of Cincinnati, OH.
- P. Saiyasitpanich, T.C. Keener: [2003] Diesel particulate emissions: Measurement and control, Student poster, Alumni home coming event, University of Cincinnati, OH.
- P. Saiyasitpanich, T.C. Keener: [2002] Control of diesel emissions using a novel wet electrostatic precipitator, Student poster, A&WMA 96$^{th}$ annual conference, San Diego, CA, 2002.

<u>To be published: Journal publications related to the specific aim of characterization of DPM emissions</u>

- Z. Liu, M. Lu, M. E. Birch, and F. Liang, "Investigation of Organic DPM Sampling Artifacts of a High-volume Sampling System", to be submitted to *Atmos. Environ.*.
- F. Liang and M. Lu, "The Load Variations of the Organic Composition of Diesel Emissions", to be submitted to *EST*.

To be published: Journal publications related to the specific aim of development of control technology

- P. Saiyasitpanich, T.C. Keener, S-J. K., M. Lu, F. Liang. Control of diesel gaseous and particulate emissions with a tube-type wet electrostatic precipitator, J. Air & Waste Manage. Assoc. 2006, Submitted.
- P. Saiyasitpanich, T.C. Keener, S-J. K., M. Lu. Removal of diesel particulate matter (DPM) in a tubular wet electrostatic precipitator. J. Electrostatics. 2006, Submitted.

**Inclusion of gender and minority study subjects: N/A**

**Inclusion of Children: N/A**

**Materials available for other investigators:**

The research data and results are accessible from various journal and conference proceedings published. Two PhD dissertations and one MS thesis are also available from the Univ. of Cincinnati library, which contain more details of the study. The prototype CESP will be tested by the NIOSH research laboratory in Pittsburgh at their Laky Lynn facility to evaluate its effectiveness in DPM control. It is also available for testing by other institutions and/or industry upon request.

Form Approved Through 9/30/2007
OMB No. 0925-0001

**Department of Health and Human Services**

# Final Invention Statement and Certification

*(For Grant or Award)*

DHHS Grant or Award No.

R01 OH007679

**A.** We hereby certify that, to the best of our knowledge and belief, all inventions are listed below which were conceived and/or first actually reduced to practice during the course of work under the above-referenced DHHS grant or award for the period

September 1, 2002 *original effective date* through August 31, 2006 *date of termination*.

**B. Inventions** (Note: If no inventions have been made under the grant or award, insert the word *"NONE"* under Title below.)

| NAME OF INVENTOR | TITLE OF INVENTION | DATE REPORTED TO DHHS |
|---|---|---|
| | None | |
| | | |
| | | |
| | | |
| *(Use continuation sheet if necessary)* | | |

**C. First Signature** —The person responsible for the grant or award is required to sign (in ink). Sign in the block opposite the applicable type of grant or award.

| TYPE OF GRANT OR AWARD | WHO MUST SIGN *(title)* | SIGNATURE |
|---|---|---|
| Research Grant | Principal Investigator or Project Director Mingming Lu, PhD | |
| Health Services Grant | Director | |
| Research Career Program Award | Awardee | |
| All other types (*specify*): | Responsible Official | |

**D. Second Signature** — This block ***must*** be signed by an official authorized to sign on behalf of the institution.

Title
Director, Sponsored Research Services

Typed Name
Tana Housh

Signature
Tana Housh

Date
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