

COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

March 1, 2020

Honorable Members of the House and Senate Education Committees
State Capitol
200 East Colfax
Denver, CO 80203

Re: Annual Report of the Colorado Higher Education Competitive Research Authority (CHECRA)

Dear Representatives and Senators:

Colorado Revised Statute §23-19.7-103(3) requires the Colorado Higher Education Competitive Research Authority (CHECRA), housed at the Colorado Department of Higher Education, to report annually to the Education Committees of the Colorado House of Representatives and Senate on research projects funded by the CHECRA in the previous calendar year. This letter reports on activities and projects funded in calendar year 2019.

The CHECRA was created to provide a source of matching funds for National Science Foundation (NSF) and other competitive federal grants that require or benefit from a state match. CHECRA funding has helped to bring significant research dollars to Colorado. CHECRA spent almost \$1.4 million in 2019 to support five multi-year research grants that jointly are bringing over \$50 million in research dollars to the state. Following is a list of the multi-year research grants that received CHECRA funding in 2019:

University of Colorado (CU)

1. In 2014, the NSF awarded the University of Colorado a six-year, \$22.8 million grant to continue and expand its Soft Materials Research Center into a full Materials Research Science and Engineering Center (MRSEC), one of the NSF's most prestigious awards. This Center focuses on work related to DNA nano-science and liquid crystal frontiers, an area where the University of Colorado is among the leading authorities. The CHECRA has pledged \$400,000 per year for six years; 2019 was the sixth year of funding.
2. In 2016, with CU Boulder as the lead awardee, the NSF awarded a \$24 million, 5-year grant for the Science and Technology Center on Real-Time Functional Imaging (STROBE).

STROBE brings together universities, national laboratories, industry and international partners to create a powerful new set of real-time imaging modalities. CHECRA has pledged \$400,000 for five years; 2019 was the fourth year of funding.

Colorado School of Mines (CSM)

3. The Colorado School of Mines, along with Colorado State University, is part of the Institute for Advanced Composites Manufacturing Innovation, a consortium of 122 companies, nonprofits, universities, and research laboratories that are partnering with the federal government to create a manufacturing hub focused on U.S. leadership in next-generation materials. Approximately \$2 million of this grant to the consortium is a direct financial benefit to the School of Mines. Recognizing the importance of this large initiative, as well as the number of players involved, CHECRA has pledged a limited cost share of up to \$100,000 per year for five years, beginning in 2015. CHECRA made the fifth of five payments of \$100,000 in 2019 to the School of Mines.
4. The NSF renewed the Colorado School of Mines' Re-inventing the Nation's Urban Water Infrastructure (ReNUWIt) Engineering Research Center, a \$5.7 million grant for which CHECRA agreed to provide a continued cost share of \$400,000 per year for five years. CHECRA made the fourth of five payments in 2019. With this grant from the NSF, the School of Mines joins leading universities in tackling acute water problems and needed infrastructure changes in the West.

Colorado State University (CSU)

5. Colorado State University received a \$5.5 million Advanced Research Projects Agency-Energy (ARPA-E) grant under its rhizosphere observations optimizing terrestrial sequestration program. This work will improve predictions of soil greenhouse gas emissions and long-term carbon sequestration. CHECRA provided the third of three payments in 2019; the payment was \$99,183.

In addition to the payments listed above, the CHECRA provided \$300,000 as a cost share for the following Major Research Instrumentation (MRI) grant received from NSF in 2019. These one-time grants provide higher education institutions with major instrumentation that supports the research and research training goals of the institution and are also used by other researchers regionally or nationally.

- The School of Mines acquired a Raman imaging Scanning Electron Microscope / Focused Ion Beam instrument, the first of its kind in a user facility. This instrument is capable of imaging materials from the millimeter to the nanometer scales, measuring and mapping elemental composition, and identifying and mapping the bonding aspects of the elements such as phases crystal quality, and strain.

Appendices to this report include detailed information on each of the projects listed above. In addition to the millions of dollars in federal funding coming into the institutions and the state—and the impressive scientific results achieved under the projects—the research centers funded by

CHECRA positively impact Colorado. As noted in the attached appendices, these benefits include support for graduate and undergraduate students, outreach to K-12 students and teachers and economic development benefits from spin-off technologies and companies.

Following are some highlights of these benefits to Colorado. We also bring to your attention Appendix A, which highlights additional benefits from the University of Colorado's Education Projects in collaboration with Fort Lewis College in the Four Corners Region of the state.

- Colorado State University's work under the ARPA-E grant is promoting CSU as a drought research facility. The work with Colorado corn farmers will contribute to our knowledge of incentives that will increase drought adaptive and root enhanced maize varieties.
- The Colorado School of Mines ReNUWIt Center has continued its collaboration with the City and has a new collaboration with the Southeast Metro Stormwater Authority. In addition, ReNUWIt has an active outreach effort, including working with K-12 teachers and schools, introducing 3rd graders to water treatment, and working to support elementary school science programs and organizations such as "Girls Lead the Way."
- The School of Mines' Advance Composites Institute is exposing Colorado's intellectual and industrial resources in wind technology to a vast array of industry partners and has secured large-scale investment from industrial partners. This is demonstrated by the development of the state-of-the-art CoMET facility at the National Wind Technology Center for wind turbine blade research and fabrication and the opportunity created for local industry and companies to use the School of Mines' extensive background in polymer science and state of the art facilities for mechanical testing.
- The University of Colorado's STROBE project is partnering with Fort Lewis College (a non-tribal native American serving institution) to create a diverse and inclusive community that focuses on cutting edge material science. In addition to the research goals, the partnership is 1) enhancing the introduction STEM classes that all Fort Lewis College STEM majors take; 2) conducting outreach to middle schools in the 4-corners region, where some schools have never had an outreach activity; and 3) carrying out workshops for teachers to enhance their ability to teach to the NGSS standards.

During calendar year 2019, the Authority received a single distribution of Limited Gaming Funds of \$2.1 million. Interest earnings on its funds totaled \$92,425 for a total income of \$2,192,425 in 2019. Expenses totaled \$1,699,183.

Thank you for your support of this ongoing research. We welcome any questions.

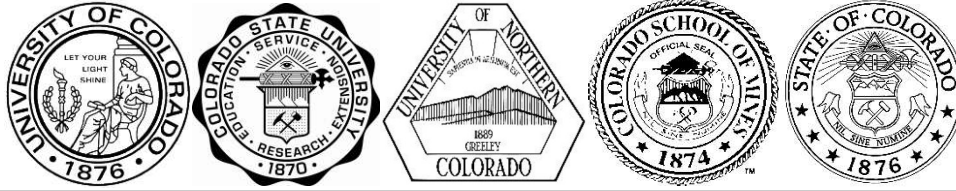
Sincerely,


for Dr. Angie Paccione
Executive Director, Colorado Department of Higher Education

Cc: Dr. Alan Rudolph, Vice President for Research, Colorado State University and Vice Chair, CHECRA
Dr. Terri Fiez, Vice Chancellor for Research, University of Colorado Boulder
Colorado School of Mines
Dr. Stefanie Tompkins, Vice President for Research and Technology, Colorado School of Mines
Dr. Andrew Feinstein, President, University of Northern Colorado

Attachments:

- Appendix A: University of Colorado STROBE/CHECRA Education Projects Collaboration with Fort Lewis College Overview
- Appendix B: University of Colorado Science and Technology Center on Real-Time Functional Imaging (STROBE)
- Appendix C: University of Colorado Soft Materials Research Science and Engineering Center
- Appendix D: Colorado School of Mines Institute for Advanced Composites Manufacturing Innovation
- Appendix E: Colorado School of Mines Re-inventing the Nation's Urban Water Infrastructure (ReNUWIt) Engineering Research Center
- Appendix F: Colorado School of Mines Acquisition of Raman Imaging Scanning Electron Microscope / Focused Ion Beam Instrument
- Appendix G: Colorado State University ARPA-E
- Appendix H: Colorado State University Acquisition of Maskless Lithography System



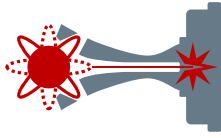
COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

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Appendix A



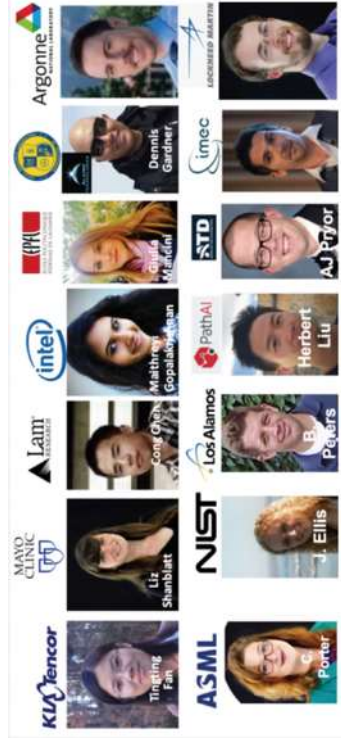
STROBE Education and Broadening Participation Enabled by CHECRA Support



Training the STEM Workforce of the 21st Century



- Introduction to STROBE Education Activities
- Education Thrust II: Transdisciplinary Graduate Pathways
- Education Thrust I: Undergraduate Pathways to STEM
- Education Thrust III: K-12 Pathways



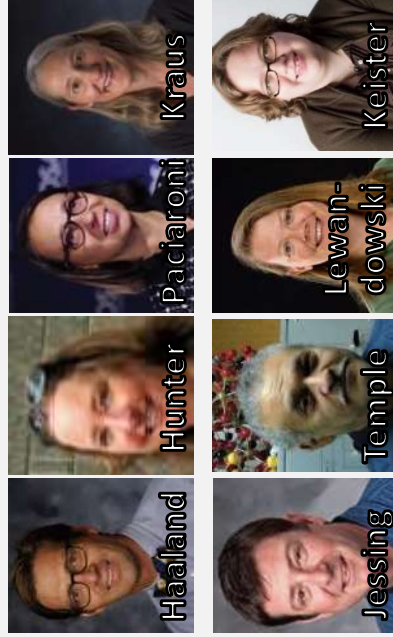
STROBE Education Goals



Thrust 1: Undergraduate Pathways to STEM

Closely coordinated partnerships and programs that increase the overall number and success of a diverse group of students in STEM, especially women, first-generation university students, and underrepresented minorities.

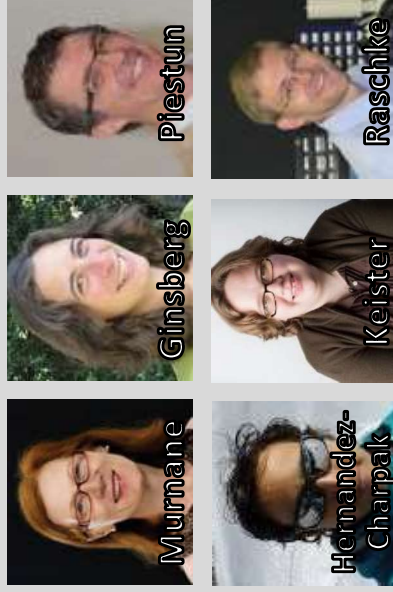
Key Personnel:



Thrust 2: Transdisciplinary Grad Education

Transformative graduate programs in imaging science that are adapted to current and future students and career opportunities. Enhanced capacities and broad skill sets of all STROBE members around communication and collaboration.

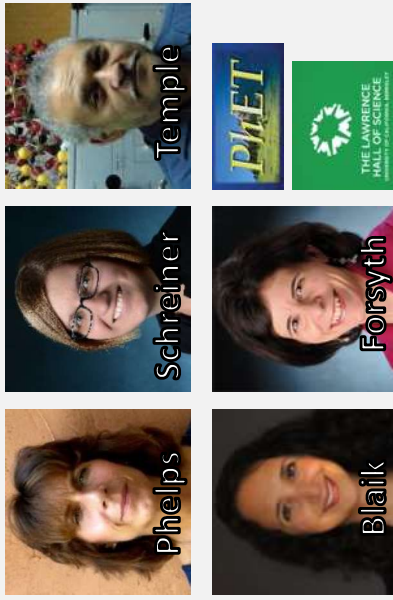
Key Personnel:



Thrust 3: K-12 Pathways

Partnerships and programs that provide STROBE-research inspired materials, activities, and educational tools to diverse communities of teachers to increase recruitment and retention of diverse groups of students in STEM.

Key Personnel:



Highlights of STROBE's Integrated Education Programs



PROJECT #1: Co-development and Enhancement of Introductory STEM classes and labs at Fort Lewis College (FLC, Durango)

- Collaborative with Fort Lewis - Native American-Serving Institution with highest number of Native American and Alaskan Native STEM students in US
- Opportunity: Increase Retention and Graduation Rates of Physics & Eng. Majors
- Culturally responsive co-development of intro classes taken by all STEM students
- Faculty, postdoctoral scientists, students and staff from FLC and Boulder
- Informed by CU Boulder Physics Education Research best practices



Prof. Heather Lewandowski



Dr. Alex Werth



Prof. Jeff Jessing



Grand Challenges in K-12 Education and Outreach



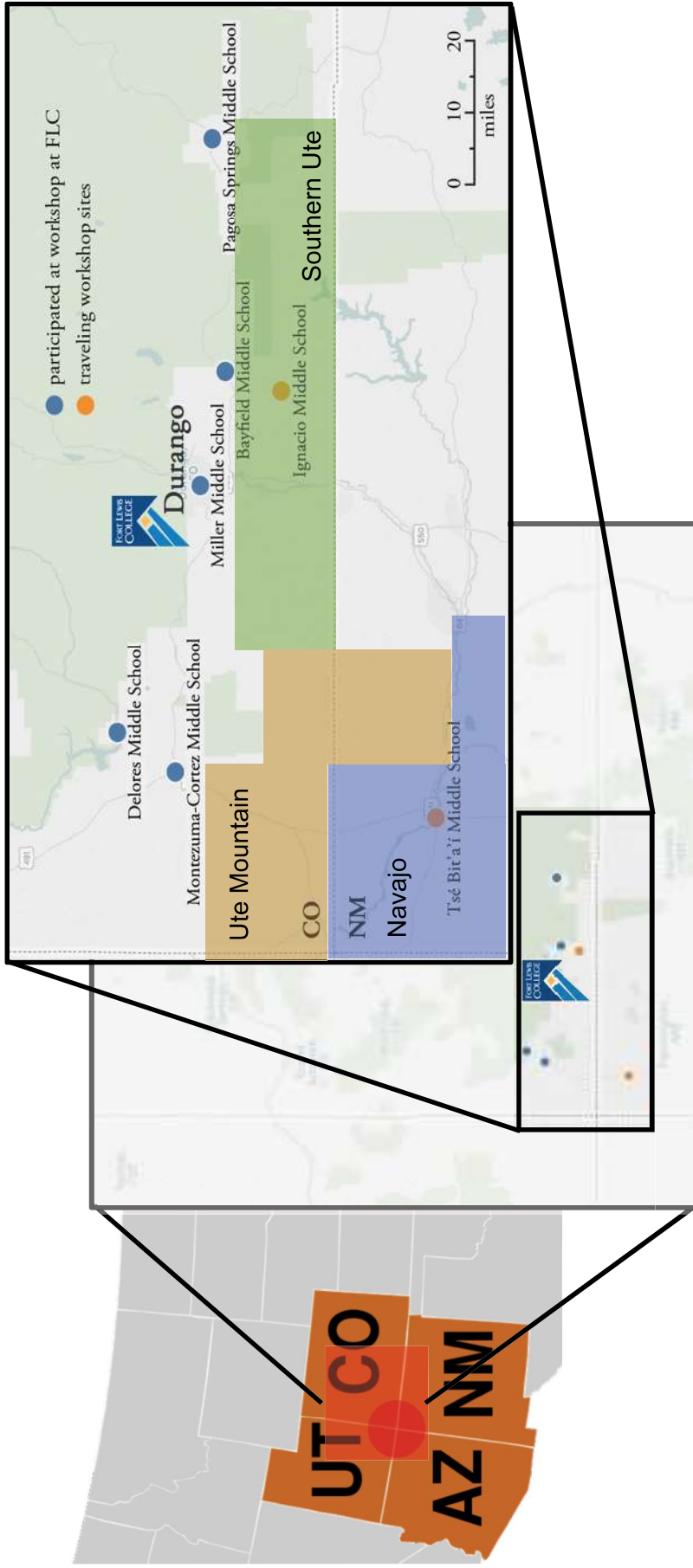
Implementation of NGSS (Next Generation Science Standards)

- Overturning siloed science
- Presenting science in the context of phenomena
- Emphasizes cross cutting topics
- Multi-year learning plans

Overcoming Barriers into STEM



- Resources (financial, time, etc.)
- Proximity to university
- Role models
- Stereotypes

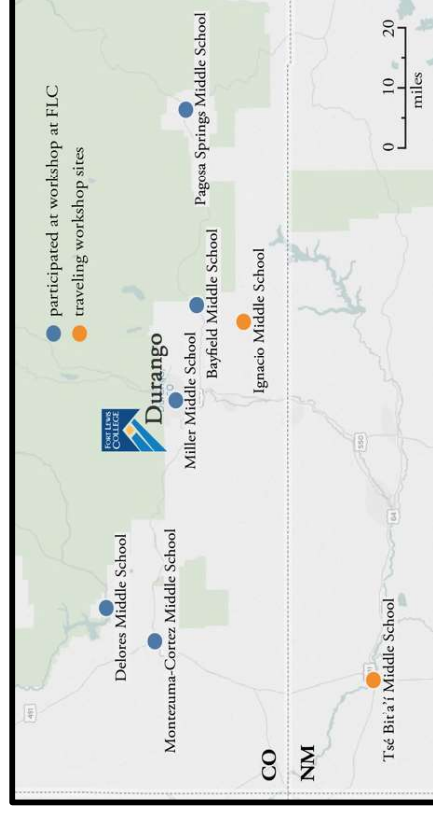
STROBE Outreach in the Four Corners Region



Four Corners Travelling Workshop Goals and Accomplishments

Created in partnership with  **Science Discovery**
UNIVERSITY OF COLORADO BOULDER

- Created in partnership with  **Science Discovery**
UNIVERSITY OF COLORADO BOULDER
- Designed to expose students to relevant STROBE content
- Impacted >700 rural middle school students (>400 in 2018, >300 in 2019)
- Engaging, hands on activities and experiments
- Gave the opportunity for FLC undergraduates to be workshop facilitators
- Opportunity to keep students engaged in high school through PEAQS 



PROJECT #3: STROBE Teacher Professional Development Workshop

Integrate Outreach, Education, Diversity, and Research Expertise Across STROBE



Create an adaptable workshop for middle school teachers

Integrate STROBE-research related classroom activities

Create a prototype teacher kit for lending library

Prepare teachers to meet the new NGSS standards in their classroom

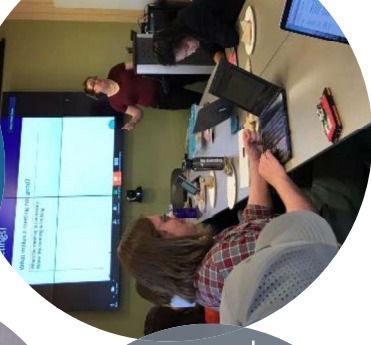
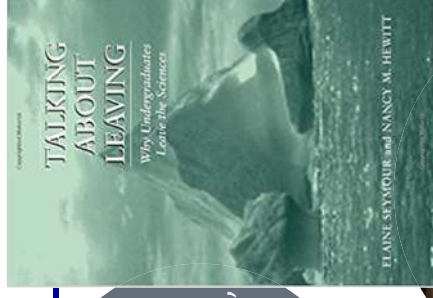
Four Corners Professional Development Workshop Accomplishments

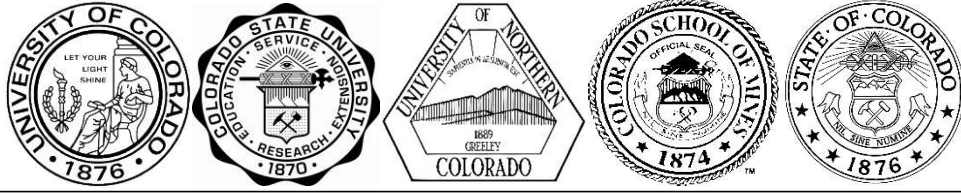
- Impacted 15 teachers
- Integrated STROBE and PEAQS research related classroom activities
- Included NGSS standards discussions and planning
- Provided teachers with prototype supply kit
- Gave STROBE and PEAQS undergraduates opportunities to facilitate and present
- Built STROBE community in Four Corners Region



STROBE Best Practices based on APS CSWP, NAS, SMART, COACH, team experience

- Community building
- Mentor training
- Team projects: academe, industry, natnl labs
- Exchanges, engagement
- Professional respectful environment
- Role models at all levels
- Alumni network
- New curricula prepare for 21st century careers
- Soft skills development
- Well-designed, meaningful, undergraduate research
- Outreach training
- Expert evaluation





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Appendix B

NSF award to University of Colorado, Boulder (UCB)**NSF Award: 1548924**

Title: Science and Technology Center on Real-Time Functional Imaging (STROBE)

Period of Performance: 10/01/2016 – 09/30/2021 (\$24M over 5 yrs pending satisfactory progress)

Total 2019 CHECRA Funding: \$400,000

Award PI's: Margaret Murnane, Jianwei Miao, Rafael Piestun, Markus Raschke, Naomi Ginsberg

Project Overview:

Microscopy and imaging are critical for discovery and innovation in science and technology, accelerating advances in materials, bio, nano and energy sciences, as well as nanoelectronics, data storage and medicine. Although electron, X-ray and optical nano imaging methods are all undergoing revolutionary advances, no single imaging modality can address critical questions underlying much of science and technology in the 21st century. These grand challenges include: How do local (atomic scale) and extended (mesoscale) structure and interactions determine material properties and function? How to directly observe magnetism on all relevant length and time scales, ranging from Å-to-nanometers (exchange length) to femtoseconds (exchange splitting) on up? What is the 3D atomic structure of glasses and how do the atoms rearrange themselves during the glass transition? Addressing these major scientific challenges requires the development of new multimodal multiscale imaging approaches by integrating state-of-the-art microscopes, new methods, novel sample preparation, fast detectors, big data, advanced algorithms and machine learning - which could not be accomplished without a center.

The NSF STC on Real-Time Functional Imaging (STROBE) is addressing critical imaging science challenges associated with five important material classes: Amorphous, Magnetic, 2D, Molecular and Bio materials. For synthesis, discovery, innovation and next-generation applications of these materials, new approaches are needed to precisely and routinely determine the atomic structure, defects, interfacial and surface morphology, magnetic and phase order/topology, as well as the transport properties and dynamic responses, in order to link structure and function. However, no single imaging modality can span the many orders of magnitude of length and time scales required to address these challenges – from sub-Å to cm, and attosecond to static. Moreover, X-ray, electron, and optical imaging have different contrast mechanisms, making them sensitive to different structural, magnetic, vibrational, and other sample properties. Fortunately, multimodal multiscale imaging using electrons (Thrust I), X-rays (Thrust II), and IR-to-UV light (Thrust III), when integrated with fast detectors, advanced algorithms, big data and machine learning (Thrust IV), can address these challenges.

The Vision of STROBE is to transform imaging science and technology by developing the microscopes of tomorrow. The Mission of STROBE is to create powerful and broadly-applicable real-time nano-to-atomic scale imaging modalities to advance imaging science and increase access, that can be used to address grand challenges in science and technology, while building a diverse STEM workforce.

Our strategies have been very successful – over the last 3.25 years, STROBE has published >122 peer-reviewed papers in journals such as Science, Nature, Nature Materials, Nature Photonics, Science Advances, Nature Communications and Physical Review Letters with >865 citations. Most importantly, a diverse group of STROBE trainees who are experts in a range of imaging techniques are in extremely strong demand by academia, national laboratories and industry. To date, 11 trainees have become faculty members in academia and 27 have been hired into national

laboratories and industry. A key to this success was to develop a network of alumni and partners, to advise students who otherwise might not have an accessible support network. Of these trainees, ~30% were women and 10% URM – well above the US national averages in physics.

Since STROBE's inception, we have integrated broader impacts into all our research, education and knowledge transfer efforts. STROBE is very diverse: 43% of the faculty, 35% of graduate students, 68% of undergraduates, 21% of the postdocs, and 100% of the STROBE staff are women or underrepresented in STEM, which represents a participation well above the national averages (in physics, the national averages are <20% (women) and <8% (URM)).



Fig. STROBE trainees bring unique skills to industry, academe and national labs, with 75% in the US.

Project benefits to the state of Colorado and the US (Include support for graduate and undergraduate students, outreach to K-12 students and teachers, spin-off technologies and companies):

STROBE brings together academia (CU Boulder, UCLA, UC Berkeley, UC Irvine, Florida International University and Fort Lewis College), national laboratories (LBNL, ORNL, NIST) and US industries to develop and advance multimodal multiscale imaging methods. STROBE brings several benefits to the State of Colorado and is very cognizant of the great opportunity this project represents for science, education, outreach to K-12 students and teachers, as well as spin-off companies and partnerships with existing local industry, universities and national labs. In the first 3.25 years of STROBE, the following activities benefitted the state –

- STROBE is addressing key EBP needs and grand challenges that are widely recognized – the need for a better connection between education and STEM workforce needs, new graduate curricula that include team science and enhanced professional development training to meet 21st century science and technology challenges, better persistence and diversity in STEM majors and careers through widespread access to good mentoring and more-inclusive pedagogy, better designed undergraduate research experiences, and outreach programs for STEM in underserved rural regions such as the four corners area. Addressing these grand challenges is critical: as one surprising example, the % female students earning bachelor's degrees in physics has not changed since 2000, at <20%.
- The STROBE Research and Education Team came together to design and submit a successfully-funded grant for a Partnership in Research and Education for Materials (PREM) for Functional Nanomaterials. Professors Ryan Haaland and Jeff Jessing from Fort Lewis College (FLC) led the PREM proposal - a strong partnership between FLC, Norfolk State University (NSU) and STROBE. This collaboration integrates education and research across FLC (a non-tribal Native American Serving Institution), NSU (a member of the Historically Black Colleges and Universities), and STROBE. The goals for PREM are to create a diverse and inclusive community that focuses on cutting edge material science that explores the multi-scale interplay of atomic and meso-scale structure and emergent physical phenomena; exciting applications that attract a diverse group to STEM; novel and effective curricula and pathways that recruit and retain the best in STEM; and long-term assessment to improve strategies and share best practices. This resulted in a \$3.6M PREM grant from NSF over 6 years, for which we are delighted.

STROBE is funding a joint postdoctoral scientist (Dr. Alex Wurth, joint between CU Boulder and FLC) who is working with students at FLC and CU Boulder to enhance the undergraduate physics laboratories at FLC, in order to attract and retain more students to STEM fields.

- STROBE nodes at Boulder and UCLA (Musumeci, Miao) developed an NSF Major Research Infrastructure proposal for a multimodal hybrid photon-electron functional imaging system, to allow for an unprecedented functional multi-scale characterization of complex samples. We are very happy that this proposal was funded at \approx \$3.3M, as it is allowing STROBE to develop new hybrid imaging concepts to address materials science grand challenges.
- STROBE and CHECRA funds are supporting \approx 20 students, postdoctoral scientists and staff in Colorado.
- Through strong Knowledge Transfer partnerships with academia, national laboratories and industry, STROBE methods and tools are now being adopted by others to address challenging materials problems. For example, STROBE is enhancing several national facilities at LBNL, ORNL and NIST through new methods and microscopes, and also working closely with industry to enhance access for other scientists to advanced new techniques. NIST Boulder laboratories is using technologies developed by the Boulder STROBE PIs (commercialized through KMLabs).
- STROBE is partnering with Science Discovery at CU Boulder to augment K-12 workshops for students and teachers that are delivered around the State of Colorado, with particular emphases on reaching middle and high school teachers and students in the four-corners region.
- STROBE industry members Ball Aerospace (Boulder) and Cymer-ASML (San Diego) are providing funds for student professional development and innovation competitions.
- STROBE is offering unique professional development opportunities for students in project and people management, social intelligence, and leadership, that are not usually offered to students in the Physical Sciences, and are attracting non-STROBE participants.
- New transdisciplinary graduate programs in imaging science are now available at CU Boulder, to better prepare students for the 21st century workplace, with students already enrolled.
- STROBE is developing methods to characterize samples provided by Intel, Ball, IMEC, IBM and elsewhere, that are challenging to characterize using other techniques. These bring many opportunities for students for internships, permanent positions and for knowledge transfer.
- Colorado students and faculty have won many prizes, awards and fellowships.

STROBE Colorado Publications from 2019 (STROBE.colorado.edu):

1. B. Metzger, E. Muller, J. Nishida, B. Pollard, M. Hentschel, M.B. Raschke, “Purcell-Enhanced Spontaneous Emission of Molecular Vibrations, *Physical Review Letters* **123**, 153001 (2019).
2. Y. Li, W. Li, M. Wojcik, B. Wang, L.C. Lin, M.B. Raschke, K. Xu, “Light-Assisted Diazonium Functionalization of Graphene and Spatial Heterogeneities in Reactivity”, *Journal of Physical Chemistry Letters* **10**, 4788 - 4793 (2019).
3. B.T. O’Callahan, M. Hentschel, M.B. Raschke, P.Z. El-Khoury, S. Lea, “Ultrasensitive Tip- and Antenna-Enhanced Infrared Nanoscopy of Protein Complexes,” *Journal of Physical Chemistry C* **123**, 17505 - 17509 (2019).
4. S.C. Johnson, E.A. Muller, O. Khatib, E.A. Bonnin, A.C. Gagnon, M.B. Raschke, “Infrared nanospectroscopic imaging in the rotating frame,” *Optica* **6**, 424 (2019).
5. O. Tzang, E. Niv, S. Singh, S. Labouesse, G. Myatt, R. Piestun, “Wavefront shaping in complex media with a 350 kHz modulator via a 1D-to-2D transform,” *Nature Photonics* **13**, 788, (2019).
6. O. Tzang, D. Feldkhun, A. Agrawal, A. Jesacher, R. Piestun, “Two-photon PSF-engineered image scanning microscopy,” *Optics Letters* **44**, 895 (2019).

7. D. Feldkhun, O. Tzang, K.H. Wagner, R. Piestun, "Focusing and scanning through scattering media in microseconds," *Optica* **6**, 72 (2019).
8. Yuan Hung Lo, Chen-Ting Liao, Jihan Zhou, Arjun Rana, Charles S Bevis, Guan Gui, Bjoern Enders, Kevin M Cannon, Young-Sang Yu, Richard Celestre, Kasra Nowrouzi, David Shapiro, Henry Kapteyn, Roger Falcone, Chris Bennett, Margaret Murnane, Jianwei Miao, "Multimodal x-ray and electron microscopy of the Allende meteorite", *Science Advances* **5**, eaax3009 (2019).
9. T. D. Frazer, J. L. Knobloch, K. M. Hoogeboom-Pot, D. Nardi, W. Chao, R. W. Falcone, M. M. Murnane, H. C. Kapteyn, J. N. Hernandez-Charpak, "Engineering nanoscale thermal transport: Size- and spacing-dependent cooling of nanostructures," *Physical Review Applied* **11**, 024042 (2019).
10. Robert Schoenlein, Thomas Elsaesser, Karsten Holldack, Zhirong Huang, Henry Kapteyn, Margaret Murnane and Michael Woerner, "Recent advances in ultrafast X-ray sources", *Phil. Trans. R. Soc. A* **377**: 20180384. (2019).
11. Begoña Abad, Joshua L. Knobloch, Travis D. Frazer, Jorge N. Hernández-Charpak, Hiu Y. Cheng, Alex J. Grede, Noel Giebink, Thomas E. Mallouk, Pratibha Mahale, Nabila N. Nova, Andrew A. Tomaschke, Virginia L. Ferguson, Vincent H. Crespi, Venkat Gopalan, Henry C. Kapteyn, John V. Badding, Margaret M. Murnane, "Nondestructive measurements of the mechanical and structural properties of nanostructured metalattices", in review (2020).
12. Yuan Hung Lo, Jihan Zhou, Arjun Rana, Christian Gentry, Drew Morrill, Young-Sang Yu, Chang-Yu Sun, Richard Celestre, Kasra Nowrouzi, David Shapiro, Henry Kapteyn, Margaret Murnane, Pupa U. P. A. Gilbert, and Jianwei Miao, "X-ray linear dichroic ptychography", in review (2020).
13. S. Hyater-Adams, C. Fracchiolla, T. Williams, N. Finkelstein, K. Hinko, "Deconstructing Black physics identity: Linking individual and social constructs using the critical physics identity framework," *Physical Review Physics Education Research* **15**, 020115 (2019).
14. R. Hoehn, J.D. Gifford, N.D. Finkelstein, "Investigating the dynamics of ontological reasoning across contexts in quantum physics," *Physical Review Physics Education Research* **15**, 010124 (2019).



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Appendix C

NSF award to University of Colorado, Boulder (UCB)

NSF Award DMR-1420736 (Previously DMR-0820579)

Title: Soft Materials Research Center

Period of Performance: 11/1/14 – 10/31/20

Total 2018 CHECRA Funding: \$400,000/ Total CHECRA Grant: \$400,000 per year for 6 years

Award PIs: Noel A. Clark, David M. Walba, Christopher N. Bowman, Jennifer N. Cha

SUMMARY

The Liquid Crystal Materials Research Center (LCMRC or the Center) has existed on the University of Colorado – Boulder campus since the early 1980s, with block funding from the NSF Division of Materials Research since September 1993. The LCMRC is currently funded as an NSF Materials Research Science and Engineering Center (MRSEC), one of an elite national network of advanced materials research programs.

DESCRIPTION OF THE PROJECT, PRINCIPAL PERSONS OR ENTITIES INVOLVED IN THE PROJECT

A major theme of materials science as we enter the 21st century is understanding and manipulation of the interactions between self-organizing complex molecules. It is precisely here that the study of liquid crystals has the greatest impact. Nowhere else are the requirements for understanding the delicate interplay between molecular architecture and its macroscopic manifestations more demanding than in the directed design of liquid crystals.

The Liquid Crystal Materials Research Center is one of the principal centers of liquid crystal study and expertise in the world, its research spanning the range from cutting-edge, basic liquid crystal and soft materials science to the development of enhanced capabilities for commercially important electro-optic, nonlinear-optic, chemical, biological, and other novel applications. The Center is a unique venue worldwide for research on key aspects of liquid crystal science and technology, chief among these the science and application of ferroelectric liquid crystals. The core Center research program is at the University of Colorado, Boulder.

The Center's research is organized within an Interdisciplinary Research Group addressing three major project themes: 1) understanding the relationship between molecular structure and macroscopic materials structure and properties of liquid crystals; (2) inventing new and useful ways of controlling liquid crystal behavior through interaction with surfaces; and (3) inventing and exploring new polymer materials possessing unique properties deriving from liquid crystallinity. Each of these research themes integrates *molecular modeling and design, chemical synthesis, physical studies, and applications development* into a multidisciplinary, collaborative research effort.

In 2019, the CHECRA funding was allocated to the three focus areas of the center described in this summary – research, industrial outreach, and education outreach.

FUNDING ALLOCATED TO EACH PRINCIPAL PERSON OR ENTITY

Research - The past year of MRSEC, with NSF funding supplemented by the CHECRA matching state funds, has continued in its role as CU Boulder's single most visible materials research activity nationally and internationally. A summary of major research accomplishments is as follows:

•Discovery of Ferroelectric Nematic Liquid Crystals - We report the experimental determination of the structure and response to applied electric field of the lower-temperature nematic phase of the calamitic literature compound 4-[(4-nitrophenoxy)carbonyl]phenyl2,4-dimethoxybenzoate (RM734). We exploit its electro-optics to visualize the appearance, in the absence of field, of a permanent electric polarization density, manifested as a spontaneously broken symmetry in distinct domains of opposite polar orientation. Polarization reversal is mediated by the field-induced domain wall movement, making this phase ferroelectric, a 3D uniaxial nematic having a spontaneous, reorientable, polarization locally parallel to the director. The spontaneous polarization density saturates at low temperature at a value of $\sim 6 \mu\text{C}/\text{cm}^2$, the largest ever measured for an organic material or for any fluid, comparable to that of solid state ferroelectrics, and close to the average obtained by assuming perfect polar alignment of molecular long axes in the nematic. We find a host of striking effects driven by ultra-low applied field ($E \sim 1\text{V}/\text{cm}$), produced by the coupling of the large polarization to the birefringence and flow of a fluid nematic phase. Electrostatic self-interaction of the polarization charge renders the transition from the nematic phase mean-field-like and weakly first-order, and controls the director field structure of the ferroelectric phase. Atomistic molecular dynamics simulation reveals short-range polar molecular interactions that favor ferroelectric ordering, including a tendency for head-to-tail association into polar, chain-like assemblies with polar lateral correlations. These results indicate a significant potential for transformative new nematic science and technology based on the enhanced understanding, development, and exploitation of molecular electrostatic interaction.

Conspicuously in the background in the history of liquid crystals is the ferroelectric nematic (NF). Predicted by Debye and Born in the early twentieth century, and revisited theoretically and experimentally extensively since, in systems ranging from colloidal suspensions rods and discs to highly polar molecules, the existence of the NF phase has never been certain, and the NF has never emerged in interest or applicability from the shadow of its weaker cousin, the dielectric nematic, which has been responsible for liquid crystal displays and the portable computing revolution of the twentieth century. We have found, in a simple previously reported thermotropic material, defining evidence for ferroelectricity and a host of novel electrically-driven optical mechanical, and flow behaviors that promise to remake nematic science and technology.

•Control of Cellular Organization Using Variable Softness in 3D Bioprinting – In 3D bioprinting liquid mixtures of cells, matrix, and nutrients are selectively deposited in patterned layers to form 3D structures that mimic domains in tissues or organs. Cells are deposited together with structural components such as hydrogels and then self-organize as living entities in the environment in which they find themselves. Cells are particularly sensitive to the chemical and mechanical properties of the surfaces on which they must live, with appropriate surface rigidity being an important preference. SMRC researchers have developed techniques whereby the surface softness of deposited structural elements can be patterned along with structure. This enables the fabrication in which cellular preferences can be designed from the beginning into 3D structures. We developed a layer-by-layer 3D printing paradigm where we purposely introduce an oxygen inhibition layer between a cured polymer structure and an oxygen-permeable window to physically limit the curing thickness during the layer-by-layer construction process in stereolithography. The thickness of the cured layer under controlled oxygen inhibition becomes nearly insensitive to the exposure dosage, which instead modulates the local crosslink density and, therefore, stiffness. This new technique allows us to print 3D structures with orthogonally patterned geometry and stiffness. To demonstrate the utility of this system, the vascular smooth

muscle cells are seeded on 3D-printed extracellular matrix to investigate how the programmed micromechano- environments dictate 3D cellular organization and in vitro tissue reconstruction

•***Twist-Bend Phase of Homologous Dimers and Trimers*** – The twist–bend (TB) liquid crystal phase is the newest nematic phase, having only been identified in 2011. Still, there are many outstanding mysteries about the nature of its nanoscale organization and behavior. We have elucidated how the number of monomer units in a linear TB oligomer influences the structure of its nanoscale helix, an important TB phase structure–property relationship. While a TB dimer exhibits a temperature-dependent variation of its helix pitch, the analogous trimer features a temperature-independent helix pitch considerably shorter than that of the dimer and other known TB materials. This study illuminates the scope of possible variations that manifest in the TB phase and represents a substantial step in controlling its nanoscale behavior for technological applications. To this end we synthesized the liquid crystal dimer and trimer members of a series of flexible linear oligomers and characterized their microscopic and nanoscopic properties using resonant soft X-ray scattering and a number of other experimental techniques. On the microscopic scale, the twist–bend phases of the dimer and trimer appear essentially identical. However, while the liquid crystal dimer exhibits a temperature-dependent variation of its twist–bend helical pitch varying from 100 to 170 Å on heating, the trimer exhibits an essentially temperature-independent pitch of 66 Å, significantly shorter than those reported for other twist–bend forming materials in the literature. We attribute this to a specific combination of intrinsic conformational bend of the trimer molecules and a sterically favorable intercalation of the trimers over a commensurate fraction (two-thirds) of the molecular length. We developed a geometric model of the twist–bend phase for these materials with the molecules arranging into helical chain structures, and we fully determined their respective geometric parameters.

•***Liquid Crystal Ordering of Four-Base-Long DNA Oligomers with Both G–C and A–T Pairing*** - We report the liquid crystal (LC) ordering in an aqueous solution of four-base-long DNA oligomers 5'-GCTA-3'. In such systems, the formation of the chiral nematic (N*) LC phase is the result of a continuous self-assembly process in which double helix stability is achieved only through linear chaining of multiple DNA strands. The thermal stability of the aggregates and their LC phase diagram have been experimentally investigated, quantitatively interpreted with theoretical models and compared with recent results on four-base sequences with only G–C or only A–T pairing motifs. N* phase is found at GCTA concentration, cDNA, between 240 and 480 mg/mL and at temperature $T < 30^{\circ}\text{C}$. The twist of the nematic director is found to be left-handed with pitch (p) in the optical range, increasing with cDNA and decreasing with T .

•***Micoreactors for Abiotic Ligation of nanoRNA*** – Self-synthesizing materials, in which supramolecular structuring enhances the formation of new molecules that participate to the process, represent an intriguing notion to account for the first appearance of biomolecules in an abiotic Earth. We present here a study of the abiotic formation of interchain phosphodiester bonds in solutions of short RNA oligomers in various states of supramolecular arrangement and their reaction kinetics. We found a spectrum of conditions in which RNA oligomers self-assemble and phase separate into highly concentrated ordered fluid LC microdomains. We show that such supramolecular state provides a template guiding their ligation into hundred-base-long chains. The quantitative analysis presented here demonstrates that nucleic acid LC boosts the rate of end-to-end ligation and suppresses the formation of the otherwise dominant cyclic oligomers. These results strengthen the concept of supramolecular ordering as a pathway toward the emergence of the RNA World in the primordial Earth. In this study, we demonstrate and quantitatively characterize an abiotic reaction pathway based on supramolecular assembly that favors the formation of long linear RNA chains by ligating short RNA oligomers,

complementing our previous result on DNA 12mers. We have successfully demonstrated the templating effect of the self-assembly of RNA oligomers, by which the geometry of the supramolecular aggregates favors intermolecular reactions over intramolecular reactions, while the local packing boosts the reaction rate.

• ***Click Nucleic Acid Mediated Loading of Nanoparticles with Therapeutic Enzymes*** – The simultaneous delivery of multiple therapeutics to a single site has shown promise for cancer targeting and treatment. However, because of the inherent differences in charge and size between drugs and biomolecules, new approaches are required for colocalization of unlike components in one delivery vehicle. In this work, we demonstrate that triblock copolymers containing click nucleic acids (CNAs) can be used to simultaneously load a prodrug enzyme (cytosine deaminase, CodA) and a chemotherapy drug (doxorubicin, DOX) in a single polymer nanoparticle. CNAs are synthetic analogs of DNA comprised of a thiolene backbone and nucleotide bases that can hybridize to complementary strands of DNA. In this study, CodA was appended with complementary DNA sequences and fluorescent dyes to allow its encapsulation in PEG-CNA-PLGA nanoparticles. The DNA-modified CodA was found to retain its enzyme activity for converting prodrug 5-fluorocytosine (5-FC) to active 5-fluorouracil (5-FU) using a modified fluorescent assay. The DNA-conjugated CodA was then loaded into the PEG-CNA-PLGA nanoparticles and tested for cell cytotoxicity in the presence of the 5-FC prodrug. To study the effect of coloading DOX and CodA within a single nanoparticle, cell toxicity assays were run to compare dually loaded nanoparticles with nanoparticles loaded only with either DOX or CodA.

• ***Design of “Triphasic” Liquid Crystal Molecules that Phase-Separate into Three Mutually Incompatible Ordered Domains*** – We have begun work on an exploratory project focused on designing and synthesizing a new ionic mesogen platform containing three mutually incompatible domains (i.e., charged ionophilic–uncharged hydrophobic–uncharged hydrophilic) that would perform ordered, mutually “triphasic” separation and/or control. Typically, most known thermotropic LC and lyotropic LC structural motifs contain only two chemically distinct regions in the same molecule, which enables “biphasic” separation and average molecular ordering (e.g., hard–soft, hydrophilic–hydrophobic). Such LC behavior is analogous to ordered phase separation by AB-type block copolymers. Analogous to the more complex ordered, phase-separated structures generated by triphasic ABC-type block copolymers, the goal of this new exploratory project was to design new small-molecule thermotropic and/or lyotropic LC platforms that would have three mutually incompatible regions and hopefully perform “triphasic” separation to generate similar ordered morphologies. However, instead of using a difficult-to-synthesize uncharged perfluorinated alkyl (i.e., fluorophilic) region that would mutually phase separate against conventional hydrophobic and hydrophilic regions, our design approach was to use a more modular, charged ionophilic region with a fluorinated counterion, analogous to a tethered ionic liquid domain.

• ***Autonomous Catalytic Nanomotors Based on 2D Magnetic Nanoplates*** – Engineering the shape of nanoparticles has emerged as an effective approach for optimizing their physical/chemical properties. In particular, two-dimensional (2D) nanostructures with their high surface area/volume ratio have opened up exciting opportunities for developing advanced anisotropic materials and facilitating chemical processes that demand high levels of surface interactions. Although the great potential of low-dimensional 2D nanoswimmers has been suggested by theoretical works, very little experimental study has been undertaken thus far. Here we fabricated a low-dimensional magnetic nanomotor based on discotic barium ferrite nanoplates. We demonstrated that the “fuel-to-motion” behavior and the enhanced diffusion of nanoswimmers are not limited to just 0D nanospheres or 1D nanorods but are also applicable to

2D nanoplates. In addition, the 2D nanoswimmers showed excellent catalytic performance in removing molecular and particle stains on cloth likely due to their catalytic activity as well as active locomotion that enhanced microconvection of solution. This study validated a new self-powered nanomachine for cleaning application without any requirement of surfactants or external mechanical energy. Here, we report a 2D magnetic nanomotor that functions as a nanocleaner to efficiently and repeatedly decontaminate organic pollutants and particle stains. In contrast to conventional magnetic nanomotors enabled by electrodeposition of Fe, Ni, or Co, our magnetic nanoplatelets were built on the controlled synthesis of ferromagnetic barium ferrite (BF) nanoplates. By sputter coating with Pt, a series of Pt-coated BF nanoswimmers were prepared. Although the bubbles formed by H₂O₂ decomposition posed an imaging challenge for the study of active colloidal physics, we took advantage of the formed nanobubbles to enhance the microconvection and introduce oxidative species during the decontamination process.

Synthesis and Assembly of Click Nucleic Acid Containing PEG-PLGA Nanoparticles for DNA Delivery - delivery of both chemotherapy drugs and siRNA from a single delivery vehicle can have a significant impact on cancer therapy due to the potential for overcoming issues such as drug resistance. However, the inherent chemical differences between charged nucleic acids and hydrophobic drugs have hindered high yield entrapment of both components within a single carrier. We demonstrate here that significant encapsulation of nucleic acids is achieved within PLGA containing polymers by incorporating the use of click nucleic acids. First, CNAs were incorporated into a triblock copolymer of poly-(ethylene glycol)-b-CNA-b-lactic-co-glycolic acid (PEG-CNA-PLGA) from which polymer nanoparticles were generated. The CNA-containing polymer particles encapsulated high loadings of DNA complementary to the CNA sequence whereas PEG-PLGA alone showed minimal DNA loading. Furthermore, the dye pyrene could be successfully co-loaded with DNA in the polymer particles as well as a complex, larger DNA sequence that contained an overhang of DNA complementary to the CNA.

Sequence-controlled synthesis of CNA-2G polymers – Successful synthesis of poly(T) CNA-2G (6-atom spacing) and its positive hybridization with complementary poly(A) DNA single strand motivate us to develop sequence-controlled synthesis strategies for the CNA-2G polymers. We employed a thiol-halogen click reaction to couple two nucleobase-pendent (could be same or different types of nucleobase) monomers to afford a dimer precursor with specific sequence. After two steps of chemical modification, the customized thiol-ene dimer was formed, which could either go through the photo-polymerization to yield poly(AB) CNA-2G or further encode a third nucleobase through a thiol-ene click reaction. Moreover, the resulting trimer is still open to accept more single nucleobase to obtain an encoded tetramer, pentamer, ... etc. The human genome project revealed that many repetitive DNA structures have critical roles in human aging and disease (*e.g.* Huntington disease is caused by a CAG repeat, Friedreich's ataxia is caused by a GAA repeat). Because of the high synthetic efficiency and low cost, our sequence-controlled CNA polymers have great potential in the study of these disease.

Cytocompatibility and Cellular Internalization of PEGylated "Clickable" Nucleic Acid Oligomers (Bryant, Fairbanks, Bowman) – CNAs are promising due to their relatively simple synthesis based on thiol-X reactions with numerous potential applications in biotechnology, biodetection, gene silencing, and drug delivery. These applications include antisense gene therapy strategies, either as the antisense agent itself for treatment of diseases caused by repeat expansions or as a complexation agent for DNA delivery. In addition, they may offer many advantages over current antisense agents, such as nuclease resistance and a more facile synthesis. However, before CNAs can be realized for such applications, it is necessary to understand whether they will be compatible

with biological systems. This study investigated cytocompatibility, cell uptake properties, and interactions with subcellular organelles of CNAs in vitro. Copolymers of CNA and poly(ethylene glycol) (PEG) were synthesized to create water-soluble CNA conjugates. PEGylated CNAs functionalized with a fluorophore were incubated with cells, and cytocompatibility was determined by measuring cell metabolism. Cellular internalization was assessed by visualizing uptake with fluorescence microscopy. Finally, immunofluorescent techniques were employed to study subcellular colocalization of CNA copolymers upon internalization. The results indicate that CNA copolymers are cytocompatible and are readily internalized by cells, supporting the idea that CNAs are a promising alternative to DNA in antisense therapy applications.

Rapid Construction of a Step-Growth Polymer with Dynamic Pendant Functionalities - In an effort to improve the polymer chain length of CNAs, we have explored the possibility of creating a ‘blank slate’ polymer onto which pendant functionalities can be later introduced. To this end, we developed the *Scheme* below, a highly efficient, atom-economic, and inexpensive polymerization between divinyl sulfone and *tert*-butylcarbazate, which yields a polymer with more than 60 repeat units, alternating between sulfone and Boc-protected hydrazine moieties. After unveiling the hydrazine functionality, we can install a wide variety pendant groups, including phenyl, furan, pyrrole, pyridine, and nucleobase functionalities, all of which are derived from available aldehydes. Moreover, these pendant groups can undergo dynamic exchange with solution-phase aldehydes, which could enable the rapid construction of polymer-scaffolded dynamic combinatorial libraries.

DNA-Assembled Core-Satellite Upconverting-Metal Organic Framework Nanoparticle Superstructures for Efficient Photodynamic Therapy - This work reports the DNA-mediated assembly of core-satellite structures composed of Zr(IV)-based porphyrinic metal-organic framework (MOF) and NaYF₄:Yb,Er upconverting nanoparticles (UCNPs) for photodynamic therapy (PDT). MOF nanoparticles (NPs) generate singlet oxygen (¹O₂) upon photoirradiation with visible light without the need for additional small molecule, diffusional photosensitizers such as porphyrins. Using DNA as a templating agent, well-defined MOF-UCNP clusters were produced where UCNPs were spatially organized around a centrally located MOF NP. Under NIR irradiation, visible light emitted from the UCNPs was absorbed by the core MOF NP to produce ¹O₂ at significantly greater amounts than what could be produced from simply mixing UCNPs and MOF NPs. The MOF-UCNP core-satellite superstructures also induced strong cell cytotoxicity against cancer cells, which were further enhanced by attaching epidermal growth factor receptor (EGFR) targeting affibodies to the PDT clusters, highlighting their promise as theranostic photodynamic agents.

Industrial Outreach - •Over 1000-fold enhancement of upconversion luminescence using water-dispersible metalinsulator- metal nanostructures – SIs Park and Cha have found Rare-earth activated upconversion nanoparticles (UCNPs) which are receiving renewed attention for use in bioimaging due to their exceptional photostability and low cytotoxicity. Often, these nanoparticles are attached to plasmonic nanostructures to enhance their photoluminescence (PL) emission. However, current wet-chemistry techniques suffer from large inhomogeneity and thus low enhancement is achieved. We have reported lithographically fabricated metal-insulator-metal (MIM) nanostructures that show over 1000-fold enhancement of their PL. We demonstrate the potential for bioimaging applications by dispersing the MIMs into water and imaging bladder cancer cells with them. Our results represent one and two orders of magnitude improvement, respectively, over the best lithographically fabricated structures and colloidal systems in the literature. The large enhancement will allow for bioimaging and therapeutics with lower

excitation power densities, thus increasing the sensitivity and efficacy of such procedures while decreasing potential side effects.

•*Orthogonal Control of Structure & Softness in 3D Bioprinting* – Precise spatial organization of tissue mechanics creates heterogeneous micro-mechano-environments optimal for diverse functions such as morphogenesis and regeneration. Mechanical heterogeneity is also closely associated with development of cardiovascular disease, and breast tumorigenesis. Engineering an extracellular microenvironment (ECM) that provides the level of mechanical, structural, and biochemical heterogeneity found in native tissues is of great interest for tissue and organ replacement, drug screening, and disease modeling. Photo-labile reactions have been widely exploited to spatially soften or stiffen hydrogel structures but have been limited to twodimensional (2D) geometries and multi-stage polymerization processes. Before optical saturation, geometry and stiffness are, however, inherently intertwined in three-dimensional (3D) photopolymerization because of the different extents of light scattering and outgrowth of photopolymerization at different levels of exposures, making it fundamentally challenging to prepare complex 3D structures with independently defined heterogeneous micro-mechano-environments and geometries. Here, we develop a layer-by-layer 3D printing paradigm where we purposely introduce an oxygen inhibition layer between a cured polymer structure and an oxygen-permeable window to physically limit the curing thickness during the layer-by-layer construction process in stereolithography. The thickness of the cured layer under controlled oxygen inhibition becomes nearly insensitive to the exposure dosage, which instead modulates the local crosslink density and, therefore, stiffness. This new technique allows us to print 3D structures with gonalgonally patterned geometry and stiffness. To demonstrate the utility of this system, the vascular smooth muscle cells are seeded on 3D-printed ECM to investigate how programming can dictate 3D cellular organization and in vitro tissue reconstruction.

Education Outreach – The Center carries out a variety of education and outreach activities that aim to enhance science literacy and achievement in communities ranging from the general K-12 population to its undergraduate and graduate students. Highlights from the past year are:

•*Materials Science From CU (MSFCU)* - The Center plans to continue Materials Science from CU, its principal SMRC K-12 outreach activity. This program has been extraordinarily successful in reaching Colorado K-12 students with needed physical sciences presentations tuned for the Colorado curriculum. To date over **2,550** classes have served **96,000** Colorado K-12 students, including **80** classes to **2,100** students during this reporting period. These presentations tuned specifically to fit into the Colorado curriculum, provide an excellent way for Center faculty, graduate, and undergraduate students to share their enthusiasm about science with the community.

•*Partnership with Arrupe High School* – During 2018, the Center worked closely with Arrupe's science teacher Stephan Graham to expand its Exploring the Nanoworld MSFCU classroom program with the new theme DNA - the Messenger. The Center-wide team [post-doc Dylan Domaille (IRG2, Chem E), graduate students Albert Harguindey (IRG2, Chem E), Sam Goodman (IRG2, Chem E), Elizabeth Delesky (IRG2, Chem E), Kate Macri (IRG1 Chemistry), Alyssa Martinez-Finkle (IRG1, Chemistry), Mike Tuchband (IRG1, Physics) and undergraduate Valerie Toman (Chemistry, Metro State University)] meet regularly, developing curriculum materials including demonstrations, labs, and student handouts on the topics: introduction to natural and man-made polymers; DNA extraction; gel electrophoresis; and the societal implications of engineering new products. The team appreciated the opportunity to hone communication skills and practice conveying science topics to non-experts.

•Pathways to STEM Careers: URM Undergraduates - Pathway Partnerships Program - The Center has established research and training partnerships with three minority-serving Undergraduate Host Institutions (UHIs) having a high percentage of URM undergraduate enrollment: •California State Polytechnic University, Pomona (CPP), •Metropolitan State University of Denver (MSD), and •California State Polytechnic University, San Luis Obispo (CPSLO). The purpose of the initial partnership with CPP was to provide cross-disciplinary research experiences for minority undergraduate students and CPP faculty in Center laboratories, and to promote successful student projects at CPP. This program has now evolved into the Pathways Partnerships with the three UHIs above, and with a much more significant outcome metric, namely that 80% of the participating UHI undergraduate alumni, none of whom were considering graduate school before entering the program, are currently successful Ph.D. students at UCB, or have graduated with a Ph.D.: •Angel Martinez in the SI Smalyukh group in Physics, now a postdoctoral researcher in the Penn MRSEC; •Alyssa Martinez-Finkle, Eduardo Guzman, Lee Foley, Alicia Gamble in the SI Walba group in Chemistry & Biochemistry. •James Amarel, •Nicholas Kuehl, •Mitch Magrini, and •Vincent Nguyen are currently undergraduates in the program. Another Partnership student, •Carlos Guerra, is currently employed as a research technician before continuing on to graduate studies. • Julia Blackmon (MSD) and • Dania El-Batal (MSD) have been admitted into the 2018 REU Program.

The successful establishment of these Pathways is the result of recognizing and focusing on key elements of training, mentoring, and evaluation. The elements that have been applied overall are now summarized, although it should be noted that not all of them may apply to any given student:

Recruiting and Evaluation – Recruiting is carried out at the UHI by UHI faculty, who seek qualified undergraduate minority students interested in pursuing an REU experience. Selected students begin their research in the UHI labs in the context of the joint UHI/UCB research activities of the program, with student and advisor receiving funding from the program. The following summer, the students continue with an REU at UCB, working on the same or a related project, and pursue this further after returning to the UHI. The longer-term continuity of the research activity promotes a much deeper commitment to research by the student and allows a more in-depth evaluation of the student's abilities than is possible after a typical REU. Students may return for a second UCB REU, and in one case the student was hired as a Professional Research Assistant after graduating from the UHI and before becoming a graduate student. Students interested in graduate school and perceived to have the potential for successfully pursuing graduate-level research are encouraged to apply to graduate schools, including UCB. In the case of UCB, the student's research achievements and the faculty experience with him or her in the program are considered, enabling the student to gain either full or provisional graduate admission.

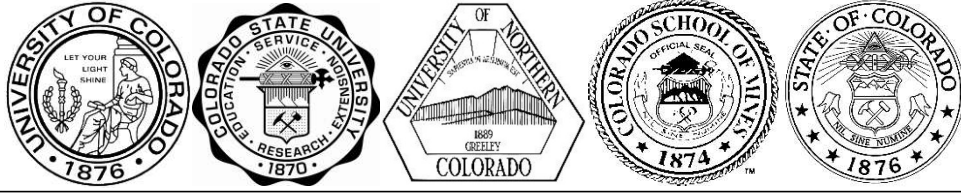
Mentoring – Once at UCB, the academic strengths and weaknesses of each UHI student are assessed and an academic program structured accordingly. The CPP students have performed well in their class-work and Ph.D. Candidacy exams, with assistance ranging from none in some cases to an intense mentoring plan including homework tutoring in others.

Research – The UHI students have become valued members of their respective research teams, having published, or on track to do so. UHI students are supported at UCB by Research Assistantship funds from MRSEC and other sources, or by departmental Teaching Assistantships. The Pathway Partnerships program demonstrates directly an effective strategy for facilitating the transition from undergraduate to graduate STEM training of capable URM

students who find themselves on academic trajectories that would not otherwise have afforded such an opportunity.. In order to encourage faculty participation, the Center has started SMRC Diversity Fellowships, which provide 0.5 year of RA support to Center SIs for a UHI or other URM student.

Pathway Partnership with Metropolitan State University of Denver (MSD) - The Center has formalized a Pathway Partnership with Metro State University of Denver, an urban university with a large URM undergraduate population. This partnership is based on the research collaboration between Prof. Ethan Tsai, an Assistant Professor in the MSD Department of Chemistry and Center graduate, with the group of Center SI D. Walba. During the academic year Tsai trains and prepares students at his lab at MSD. Research projects extending over several AYs and summers will enable evaluation and involvement of students, which, in this case, will be enhanced by the proximity of the Center (only 30 min from MSD). During the current reporting period MSD alumni Alicia Gamble and Lee Foley are now advancing to candidacy their graduate in their work as PhD students in the UCB Department of Chemistry. MSD Students Julia Blackmon and Dania El-Batal begins her Center research career as an REU in June, 2018.

•***Pathways to the Workforce Workshop*** – (organized jointly with UCSB) – The Center lead a summer a weeklong intensive, professional development activity for a diverse cadre of STEM students and postdocs from the MRSEC and PREM networks. Participants were trained to think in broad, interdisciplinary fashion and to work successfully within teams benefitting from diverse perspectives. The workshop guides participants in acquiring professional development skills, so they can transform their education into impact. Workshop participants gain valuable skills that are not taught in traditional university coursework including networking and building relationships.



COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

Appendix D

Institute for Advanced Composites Manufacturing Innovation (IACMI)

Colorado School of Mines (Mines)
CHECRA Grant: \$100,000 (per year for 5 years)
Reporting Period: January 1 - December 31, 2019

Summary:

IACMI's 4.2 Wind Turbine Technology project focuses on lower the levelized cost of wind energy while simultaneously increasing the quality and reliability of wind turbines. To this end, the project has several targets:

- 1) Decreasing mold cycle time
- 2) Integrating thermoplastic matrices into the current production process
- 3) Augmenting the robustness of fabric placement through automation
- 4) Conducting in-press nondestructive evaluations (NDE)

The main focus of the team at Mines this past year was to contribute to the first two targets in the project, but advances were also made in the area of NDE (item 4). More specifically, the CY2019 contributions made by the Mines team made several key contributions to the goal of the wind technology area. The contributions can be summarized in three main areas:

- 1) Generation and delivery of a database of mechanical properties (tension, compression, shear, fatigue) that benchmarks the performances of the new thermoplastic fiber reinforced composites against the industry status-quo thermoset composites.
- 2) Fundamental evaluation of the adhesive properties of 4 different binders (2 thermoset, 2 thermoplastic) in their ability to be used to join segments of wind turbine blades together. The fracture toughness data generated by Mines informed the selection of the adhesive used to join the 13 m wind turbine blade together that is being made in CY2019.

Additionally, 2 new projects were started late 2018 and worked on CY2019 and continue into CY2020. These are:

- 1) IACMI 4.3 – thermal joining of thermoplastic matrix, fiber reinforced composite wind turbine sections.
- 2) IACMI 6.20 – closing the loop on automotive carbon fiber prepreg manufacturing scrap

Mines contributed to these projects during CY2019 as summarized:

- 1) Evaluated 7 different thermal welding technologies and down-selected to the two most viable technologies to pursue. Developing database for inductive welding joints vs. adhesively bonded joints, as well as technologies for manufacturing scale-up of the inductively welded joints.
- 2) Characterizations (X-ray and electron microscopy) of baseline automotive pre-preg material vs. those made with Vartega (CO small business) recycled carbon fibers toward completing a qualification database.

Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity:

4.2 Project: Replacing thermoset with thermoplastic matrices in fiber reinforced composites used to construct wind blades offers the promise of reducing the levelized cost of electricity (LCOE). Thermoplastic use facilitates the end of service life recycling thus providing opportunities to create manufacturing jobs in the conversion of the reclaimed materials. The potential ability of

thermoplastics to reduce the manufacturing cycle time strongly affects LCOE and therefore provides the strongest incentive for their commercial adoption. Naturally, for thermoplastic composites to be utilized, the mechanical properties must be equivalent to thermosetting composites.

4.3 Project: With thermoplastic-based materials qualified for wind turbine blades in the 4.2 project, the 4.3 project aims to qualify further manufacturing advancements afforded by the use of thermoplastics: namely, the use of thermal welding techniques to bond pieces of the blade together and/or repair the blades. Ultimately, this technology could allow blades to be transported in smaller pieces and then joined on site, enabling larger wind turbine installations, which lead to higher efficiencies per wind turbine since the power production increases with the area swept by the wind turbine blades squared. Today, the ability to transport large blades limits larger installations – segmented joining technologies would overcome today’s limitations.

6.20 Project: This project aims to reduce the waste generated in manufacturing carbon fiber reinforced composites by qualifying the use of carbon fibers that are recycled for use in automotive pre-preg materials.

Principal Senior Investigators

Aaron Stebner

Funding from CHECRA

\$100,000

The manner in which each principal person or entity applied the funding in connection with the project

\$25,390: Summer Salary + Fringe for PI Aaron Stebner and Co-I Joe Samanuik

\$540: Supported PhD student Peter Caltagirone stipend

\$5,509: Supported administrative assistants Anna DeGraaf and Stephanie Mahoney to assist in facilitating the management of the research program.

\$15,604: went to indirect costs

\$53,175: supported the procurement of an environmental chamber that created capability for testing the composite materials in response to corrosive environments and hot and cold temperatures.

Results achieved

1. **Project 4.2** 2019, the qualification database for the thermoplastic-based composite materials for wind turbine blades was completed and accepted by manufacturers. A vast number of mechanical tests were conducted to qualify the final selected Elium resin system and various fiber layup geometries, in duplicates of at least 5, and then repeated for an epoxy resin system that is used in today’s wind turbine blades. In total, over 3,000 individual mechanical tests were conducted for the four fiber layups (*i.e.*, [0/0/0/0]₂ from 0 degree, [0/0/0/0]₂ from 90 degree, [0/90/90/0]₂ from 0 degree, and [0/90/90/0]₂ from 45 degree). Specimens were tested in tension, compression, shear, and fatigue.

2. **Project 4.2** Adhesives were selected for bonding wind turbine segments together based upon

over 300 interlaminar shear tests performed on 4 different adhesives with 3 different adhesive layer thicknesses. A full fracture toughness database was developed for all 4 adhesives.

3. **Project 4.3** Resistive and induction welding were selected as the most viable thermal joining technologies for thermoplastic wind turbine blades. A full (mode I and mode II) fracture database was generated comparing the effects of varying manufacturing parameters for these two technologies vs. properties from traditionally (adhesive) joined segments.

4. **Project 6.20** X-ray photospectroscopy was used to characterize the surfaces of recycled carbon fibers vs. freshly manufactured carbon fibers. X-ray tomography and scanning electron microscopy were used to characterize the formation of voids and ability for recycled carbon fibers to hold strong bonds to resin materials during failure of automotive prepreg materials made from recycled carbon fibers.

Publications in 2019:

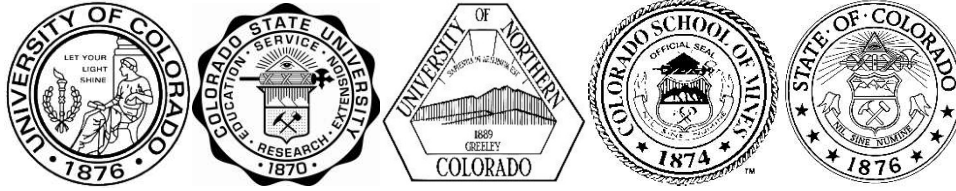
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Education and Outreach - Partial CHECRA Support

In 2019, the ICAMI project at the school of mines helped support one post-doctoral research associate, one Ph.D. graduate students, three hourly undergraduate students, and two summer undergraduate interns. Workforce development is a cornerstone of the ICAMI mission and the matching funds from CHECRA are critical in this aim.

Summary of benefits to the State of Colorado

- Support of the aforementioned research associates and students who will be highly desirable candidates for Colorado’s rapidly growing workforce in the wind energy sector
- Large-scale investment by cost matching from industrial IACMI partners to universities in the state of Colorado
- Exposure of Colorado’s intellectual and industrial resources in wind technology to a vast array of industry partners in the IACMI consortia
- Development of the state of the art CoMET facility at the National Wind Technology Center for wind turbine blade research and fabrication
- Ability for local industry and companies to use the School of Mines’ extensive background in polymer science and state of the art facilities for mechanical testing



COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

Appendix E

Engineering Research Center Reinvention of the Nation's Urban Water Infrastructure (ReNUWIt)

Colorado School of Mines

CHECRA Grant: \$400,000 (per year for 10 years, renewed)

Reporting Period: January 1 - December 31, 2019

Summary: The Engineering Research Center (ERC) for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt) at the Colorado School of Mines, under the leadership of Dr. John E. McCray, is a collaborative effort among four research universities: CSM, Stanford University, University of California at Berkeley, and New Mexico State University. The ERC was established on August 1, 2011 and is the first center to focus on civil infrastructure ever funded by the National Science Foundation.

Cities are facing a mounting water crisis from population expansion, ecosystem demands, climate change, and deteriorating infrastructure that threatens economic development, social welfare, and environmental sustainability. ReNUWIt's vision is to facilitate the transition of existing water supply systems, urban flood control, and wastewater treatment to a new state that will enhance the security and economic vitality of the nation's cities. Accordingly, the goal of this ERC is to advance new strategies for water/wastewater treatment and distribution, develop modular technologies and concepts, and prepare students to lead efforts to reinvent urban water infrastructure.

Description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity

To meet the challenges of reinventing urban water infrastructure, ReNUWIt has three research thrust areas defined as follows:

- (1) **Urban Systems Integration and Institutions:** Support the reinvention and restoration of urban water systems through the development of decision-making tools that enable sound decision making about future investments in urban water infrastructure;
- (2) **Efficient Engineered Water Systems:** Develop new, modular technologies to overcome barriers that prevent wider application of existing by underutilized technologies and collecting data on technical performance;
- (3) **Natural Water Infrastructure Systems:** Develop technologies for managing natural systems to treat and store water while simultaneously improving urban aesthetics, with focus areas in stormwater treatment for beneficial use and groundwater recharge.

Water resource planners are hesitant to integrate new types of engineered treatment systems into their water portfolio due to uncertainties about cost, reliability, public health risks, and overall impacts on system performance. Thus, a mechanism for technology assessment is needed at scales ranging from the laboratory to the full-scale service area. Such capabilities do not exist and as a result, many good ideas are not brought into practice. To facilitate the integration of new technologies into urban water systems, tools like life-cycle assessment for decision-making are being advanced as well as conducting research and implementation of engineered systems. The strategic research plan continues to evolve in response to research outcomes, supplemental funding opportunities, and new information related to achieving ReNUWIt's overarching goals.

Within the *Urban Systems Integration and Institutions* thrust, research focuses on the development of integrated regional water models. The goals of the thrust area are to: (i) develop integrated decision support systems for utility planning; (ii) develop integrated visioning, assessment, and implementation tools for regional and municipal water planning; and (iii) identifying “technology diffusion pathways” to increase the likelihood of technology implementation. Mines is examining the legal, economic and technical feasibility of beneficial use of stormwater in a redeveloping neighborhood in northwest Denver (Berkeley neighborhood) including a method to project increases in impervious areas and the subsequent impact to stormwater flows and quality.

The goal of the *Efficient Engineered Systems* research thrust is to characterize the viability of existing but underutilized technologies at different scales by assessing their economic, environmental, and social costs and benefits. The specific aims of this thrust are: (i) develop improvements to energy and resource recovery from existing municipal wastewater systems; (ii) develop or assess new processes, approaches, and practices that support direct potable reuse of municipal wastewater; and (iii) advance (i) and (ii) to pilot-scale and full-scale demonstration and adoption. Research at Mines has incorporated smart system controls to monitor/ model/ optimize the hybrid sequencing batch-membrane bioreactor (SB-MBR) system operation for nutrient management (e.g., tailored water management).

The thrust area on the use of *Natural Water Infrastructure Systems* brings a much-needed quantitative approach to an area that has not previously been subjected to rigorous engineering analysis. The realigned goals of the thrust area are to: (i) develop novel approaches for manipulating subsurface natural system unit processes to predictably enhance stormwater and treated wastewater qualities; (ii) identify new ways of designing and operating unit process to maximize water quality and flood protection while enhancing function and aesthetics; and (iii) deploying sensors and actuators for real-time control and management of processes. Research at Mines is advancing passive treatment of stormwater through bioinfiltration systems and the hyporheic zone in streams.

Within the ReNUWI framework described above, twelve projects were funded in part by CHECRA in 201:

- Feasibility for Beneficial Use of Stormwater in Denver (U2.5);
- Long-term Sustainability of Stormwater Technologies (U2.13), joint with Colorado State University;
- Predicting Urban Water Demand for Infill and Redevelopment in Denver (U2.15);
- Reclaiming Energy from Wastewater using Anaerobic Digestion (E2.4);
- Tailoring Water Reclamation for Specific Purposes (E2.9, formerly E1.1);
- Chemical valorization of Energy from BioWaste (E2.12);
- Phosphorus Recovery in Existing Wastewater Treatment Facility Infrastructure (E2.16);
- Alternative Potable Reuse Treatment Trains (E3.4);
- Smart Engineered Wetlands (N1.2);
- Stormwater Infrastructure for Water Quality (N3.3); and
- Engineering Streambeds for Water Quality Improvement (N3.4).

The table below lists project funding per project by the primary lead for each project, although several projects are co-led, as annotated below.

Principal Investigators	Funding from CHECRA
John McCray, CSM Principal Investigator, ReNUWIt Center Lead Project Lead, Feasibility of Beneficial Stormwater Use in Denver, U2.5 (Terri Hogue is co-lead) Project Lead, Long-term Feasibility of Stormwater Technologies, U2.13 Project Lead, Engineering Streambeds for Water Quality Improvement, N.3.4 (Chris Higgins is co-lead)	\$87,313 \$59,036 \$44,104
Tzahi Cath Project Lead, Tailoring Water Reclamation for Specific Purposes, E2.9	\$35,672
Linda Figueroa Project Leads, (Figueroa) Novel Phosphorus Extraction/Recovery in WWTF, E2.16	\$14,679
Linda Figueroa and Junko Munakata Marr Project Leads: Reclaiming Energy from Wastewater using Anaerobic Digestion, E2.4	\$68,227
Timm Strathmann, E.2.12, Hydrothermal Technologies to Valorize Biologically Tailored Wastewater Solids	\$8,869
Christopher Higgins Project Lead, Stormwater Infrastructure for Water Quality, N3.3	\$67,485
Terri Hogue Project Lead, Predicting Urban Water Demand in Denver, U2.15	\$55,591
Jonathan Sharp Project Lead, Smart Engineered Wetlands, N1.2	\$12,817
TOTAL SPENDING (Jan-Dec 2019)	\$453,793

Within the ReNUWIt projects (2019), full or partial support was provided to:

- 2 Post-doctoral Researchers
- 6 Doctoral students
- 5 Master's of Science Thesis students
- 16 Hourly Undergraduate and Non-thesis MS students
- 4 REUs ~ a 10 week summer program designed to provide research experience for undergraduates
- 3 Research Staff
- 9 Faculty ~ 1 Assistant Professor; 2 Associate Professors; and 6 Professors

The manner in which each principal person applied the CHECRA funding in connection with project results

John McCray, Professor: Discretionary center funding for supporting new research directions. In support of the Denver Beneficial Stormwater Use project (U2.5) CHECRA funding supported partial salary support for Dr. McCray, partial support for one post-doctoral researcher, tuition, stipend and nominal materials for one PhD student, three undergraduate students to assist with frameworks and technical research to overcome policy and legal barriers to allow stormwater beneficial use and one teaching faculty for data synthesis in development of engineering drawing at Willis Case Golf Course. This work lead to a separate research directive focused on

the evaluation of the long-term feasibility and sustainability of stormwater technologies (U2.13). In support of U2.13, CHECRA funding supported tuition and stipend for one PhD student.

One PhD student and materials supported field scale testing and implementation of engineered urban streambeds for water quality enhancement thru BEST (N3.4). As an outcome of this work, Dr. McCray secured a partnership with the City of Golden, to engineer streambeds in stormwater channels to improve water quality. Mines and Golden jointly received a Proof of Concept (POC) Innovation grant, awarded by an external technical advisory board of Colorado business entrepreneurs.

Tzahi Cath, Associate Professor: Funding for one PhD student focused on SB-MBR energy optimization and tailored non-potable reuse of treated wastewater (E1.1). The goal is to use treatment systems that are tailored to provide specific water quality needed for specific non-potable tasks, which should be more cost efficient than treating to near drinking water standards, the traditional approach for traditional urban treatment plants. This research is leveraged with a PhD student and materials supported by NSF funds.

Linda Figueroa, Professor: Funding provided support for six undergraduate students to sample and analyze the pilot scale anaerobic bioreactor at Metro Water Reclamation District (E2.4) and partial salary for Dr. Figueroa for research oversight. Outcomes from this work have transformational changed in the current wastewater treatment paradigm. Also see the project description for project E.2.16 below.

Junko Munakata Marr and Linda Figueroa, Professors. CHECRA funds supported tuition for two graduate students and hourly support for a undergraduate student working on phosphorus recovery within existing wastewater treatment facility infrastructure (E2.16). Both graduate students are currently employed with Metro Wastewater Reclamation District and are expected to directly implement research findings at the District.

Christopher Higgins, Associate Professor: Partial salary support for Dr Higgins for his leadership role as N-Thrust Leader. In addition, one undergraduate student supported work with the City of Denver to develop of a field site at Cuernavaca Park and with the City of Golden for pilot scale testing of BioCHARGE (N3.3). A post-doctoral researcher was partially supported to implement a BIOCHARGE system in the City of Fort Collins, in partnership with the City of Fort Collins.

Terri Hogue, Professor: One PhD student was fully supported for remote sensing to help understand factors affecting urban water use and projecting changes to water demand in Denver (U2.15). The broad goals this effort is to develop high-resolution remote sensing methodologies to help predict water use and manage water conservation. Another PhD student was partially supported to conduct hydrologic modeling in support of U.2.5 (above). Nominal funds (<\$500) were provided for expendable materials and supplies.

Jonathan Sharp, Associate Professor: Partial faculty salary support was provided for Dr. Sharp for his leadership roll as the Diversity and Inclusion co-Director for ReNUWIt across all partner institutions, as well as for implementing an engineered treatment wetland at the Mines Park Test site on Mines Campus.

Timm Strathmann, Professor, received general center support for ReNUWIt project E2.12 (Application of hydrothermal technologies to valorize biologically tailored wastewater biosolids). This project focuses on advancing hybrid biological-thermochemical technologies for recovering

economically valuable products from wastewater biosolids (i.e., valorizing the waste). Working closely with collaborators at the National Renewable Energy Laboratory (NREL), located in Golden, CO, we are examining multiple process pathways for producing propylene, a billion dollar chemical intermediate, from biosolids. This product has much greater financial potential than the conventional biogas product from anaerobic digestion of wastewater sludge. Two Mines PhD students, funded by non-CHECRA sources, work in laboratories at both Mines and NREL to identify stable solid acid catalyst formulations that are active for breaking down microbial products and upconverting the resulting acid monomers into propylene. The work also serves as a vehicle for inclusion of undergraduate student researchers in the state of Colorado (2 participated this past year). This work supports both the missions of ReNUWit (Transforming the way we manage urban water infrastructure systems) and NREL (advancing the science and engineering of energy efficiency, sustainable transportation, and renewable power technologies).

Results Achieved

Results from the *Urban Systems Integration and Institutions* thrust continued to focus on stormwater planning, management and treatment. In partnership with the City and County of Denver (U2.5), the technical, legal, policy and social barriers are being evaluated to enable beneficial use of stormwater runoff in the rapidly re-developing Berkeley neighborhood of west Denver. Modeling and stormwater quality sampling is being conducted for Denver to inform proposed new regulations for infill redevelopment in the City. This work involves monitoring water quality during storm flows (with a sampling and flow measurement network in the storm sewer system of the Berkeley neighborhood in west Denver. The goal is to help the city to understand whether real data, and subsequent data-based decision making, is better than traditional decision-making processes related to urban water quality and potential new regulations for new infill development. For the State of Colorado, we are working with the Colorado Water Conservation Board (CWCB) and the State Engineer's office (SEO) to develop new policy to enable increased stormwater runoff from infill development to be utilized for beneficial use. Mines received a \$50,000 grant from the National Science Foundation (NSF) to provide an internship for PhD student Ryan Gilliom with the CWCB and Colorado SEO to work on innovative policy to enable stormwater beneficial use. This work was recently codified into law by the Colorado legislature. In addition, Professor McCray received a \$60,000 grant from NSF to fund stakeholder workshops in the front range to brainstorm overcoming barriers to implementing beneficial stormwater use in the Front Range. Work by professor Hogue in U.2.15 aims to use remote sensing techniques to better understand greening (largely from urban irrigation) across the city, and to elucidate the technical and socio-economic factors that impact outdoor water use. Results from this project should be useful in developing remote sensing techniques to predict water use for various development scenarios, and also to implement and track new water conservation programs.

Results from the *Efficient Engineered Systems* research thrust continued to rely on field research on the Mines campus utilizing sequencing batch membrane bioreactor treatment of wastewater from housing at Mines (~7,000 gal/day), as well as pilot scale projects at the Metro Water Reclamation District utility in the Front Range (described in more detail below). The demonstration-scale treatment unit at Mines Park allows effluent qualities to be tailored to various reuse applications (i.e., urban landscape irrigation; streamflow augmentation; groundwater recharge) and continues to be supported through collaborations with manufacturers and start-up companies within Colorado. Identifying mechanisms (E2.9) by which nutrient removal can efficiently be achieved while lowering energy consumption is

beneficial both from an energy resource standpoint and an economic perspective. Alternatively, E2.9 also investigates strategies for optimization of generating on-demand effluent qualities with elevated levels of nitrogen while simultaneously optimizing energy demands continue.

Our demonstration scale project titled “Coupled Hybrid Anaerobic Reactors for Generation of Energy (CHARGE)” have been operating at the Plume Creek Water Reclamation Authority (PCWRA) in Castle Rock for six years to evaluate the long-term viability of generating energy from wastewater. The project involves operations considerations such that small utilities can make use of an anaerobic treatment process to generate methane that can be used for energy while eliminating the need for aeration. The results from primary anaerobic treatment have led to additional investment by NSF (\$329K; Sept 2015 – Aug 2018) and Water Environment Research Foundation (106K; May 2016 – Apr 2019).

A project to evaluate phosphorus extraction/recovery schemes and pilot scale implementation within existing wastewater treatment facility infrastructure was started in 2017 (E2.16). This project is part of an overall goal to recover valuable resources of energy and nutrients, particularly phosphorus, from wastewater. Metro Wastewater Reclamation District (District) is currently undergoing extensive upgrades to the Robert W. Hite Facility (RWHTF) to meet increasingly stringent nutrient regulations, particularly focused on effluent discharge phosphorus concentrations. Enhanced biological phosphorus removal (EBPR) is a sustainable and cost effective means to remove phosphorus from the liquid stream, however the process has been shown to negatively impact other process areas in both performance and cost. As a result, the District has continued developing near-term and potential long-term phosphorus management options, harnessing the experience of industry leaders and university expertise to make informed infrastructure and operating strategy decisions that best serve the 1.8 million Denver Metro area ratepayers. This project research will evaluate EBPR for improvements and optimization to maintain low effluent phosphorus concentrations while improving the effectiveness and efficiency of the RWHTF in other areas.

Results from the *Natural Water Infrastructure Systems* thrust continued to focus on developing smarter, more efficient methods for infiltrating recycled water for aquifer storage while simultaneously improving water quality. These sustainable technologies capitalize on the management of natural treatment processes to facilitate water treatment while enhancing storage infrastructure. For example, upscaling for field testing at the field scale of modules termed “Biohydrochemical Stream Water Treatment (BEST)” continued (N3.4). The BEST system was employed at a site by the City of Golden to mitigate stormwater runoff pollution. We are working with Golden to implement a second site. Mines received funding from the State of Colorado Innovation program to work with Golden. To our knowledge, this was the first grant given to an environmental-water project. A geomedia stormwater infiltration system (BioCHARGE) was installed by the City of Denver at Cuernavaca Park for removal of dry-weather urban drool pollutants (N3.3). An outcome from this work was the successful DoD SERDP award (\$491K; 2018 - 2020) to improve BMP stormwater treatment designs to prevent sediment recontamination. A new BIOCHARGE system has been installed in the streets of Fort Collins, in collaboration with the City of Fort Collins and the Colorado State University Stormwater Center.

Summary of Benefits to the State of Colorado

- Received \$448,256 NSF core funds in 2019. These funds in combination with CHECRA funds (\$400,000) and \$178,586 CSM matching funds have supported:
 - 43 graduate students (MS thesis and PHD tuition and stipend) in the first 8.5 years of ReNUWit (2011-2019) with degrees in Civil & Environmental Engineering,

Environmental Engineering Science, and Hydrologic Science and Engineering. Women comprised ~40% of these graduate students. Three existing graduate students and one post-doc are employed by either Metro Wastewater Reclamation District or the City and County of Denver.

- Research experiences for 48 Mines undergraduates where ~55% of these students are female and 22% are other under-represented minorities.
- Continued collaboration with the City and County of Denver, the Urban Drainage and Flood Control District (UDFCD) to predict changes in stormwater management due to urban infill and development. A new collaboration with Southeast Metro Stormwater Authority (SEMSWA) was begun in October. We expect this partnership to result in collaborations with other stormwater management utilities in the Front Range.
- Collaboration with Metro Wastewater Reclamation District and Carollo Engineers investigating potential energy savings and treatment efficiencies associated with alterations in treatment plant operation for nutrient removal.
- A biohydrochemical enhancements for streamwater treatment (aka, BEST) pilot channel has been constructed with support from the City of Golden as well as from the State of Colorado Innovation Fund through a competitive grant process. In addition, Seattle Public Utilities provided \$50k for installation recommendations for BEST stream restoration and floodplain reconnection tentatively planned for 2019.
- A new BIOCHARGE stormwater quality enhancement technology was installed near the intersection of Mountain and Walnut streets in Fort Collins. This work is part of both N.3.3 and U.2.13, and is a collaborative effort between Mines, CSU, and the City of Fort Collins.
- Research to valorize waste biosolids into valuable plastic-like products has shown promising results. This is a joint effort between Mines and NREL.
- Successful pilot scale testing of anaerobic treatment process to generate energy at the Plum Creek Water Reclamation Authority has led to plans for expanding piloting at Littleton Englewood WWTP.
- Continued success obtaining new research grants at Mines to broaden the design and implementation of ReNUWIt developed treatment systems and approaches. These grants will support graduate and undergraduate students, many of which are expected to enter or remain in the Colorado workforce.
- Bi-monthly seminars organized and sponsored by the ReNUWIt students. Seminar speakers and topics include a range of student research, industry partners, and experts.
- ReNUWIt work on engineered streambeds (Professor John McCray and PhD student Skuyler Herzog) was highlighted in a new film that premiered at the Seattle Film Festival titled: ‘Engineering With Nature – An Ode to Water, Wood, and Stone’ (produced by Leap Frog Films).
- The collaboration between ReNUWIt at Mines and the Urban Water Innovation Network (UWIN), an NSF Sustainability Research Network (SRN), at Colorado State University is underway. A student and a faculty member at Mines is working with a student and two faculty members at CSU to evaluate sustainability of ReNUWIt water green infrastructure (GI) technologies compared to traditional GI technologies.
- Two Mines student researchers earned awards or special appointments based on their ReNUWIt work in Urban Water: PhD student Kate Newhart earned 1st place in the LIFT Intelligent Water Systems Challenge. PhD Student Ryan Gilliom won the best student presentation at the annual American Water Resources Association annual meeting .
- Two Mines professors earned awards or special appointments based on their ReNUWIt work in Urban Water: Professor Terri Hogue was selected to be the Robert E. Horton

lecturer in Hydrology for the American Meteorological Society. Professor John McCray was appointed to the European Union National Academy of Sciences.

- The ReNUWIt Industrial Advisory Board (IAB) meeting for all four universities was held in Golden on Mines campus in September 2019. This included industry, consulting, utility, municipal, legislative, and non-profit stakeholders from across the front range.
- Current Director of the Colorado Water Conservation Board, Becky Mitchell, gave the keynote talk at the fall ReNUWIt IAB meeting.
- ReNUWIt gave numerous workshops, “lunch and learns”, and technical outreach talks to stakeholders in the Front Range, including City and County of Denver Department of Public Health and Environment, Department of Green Infrastructure Planning and Development, and Wastewater Management Division, the Colorado Stormwater and Floodplain Managers Association (CASFM), Wright Water Engineers, Southeast Metro Stormwater Authority (SEMSWA), Denver Water, and Colorado Stormwater Council.
- Numerous front range water professionals came to Mines to give talks and workshop at the invitation of ReNUWIt, particularly in the Environmental Engineering Seminar Series and the ReNUWIt student group (SUWIR) seminar series.
- Several outreach efforts are ongoing, including with Shelton Elementary in Golden, Lakewood High School, and numerous children’s camps. Highlights include the Shelton Elementary (K-5) Math and Science Fair, Rocky Mountain Summer Camp for Dyslexic Kids, where 40 K-6 students participated outreach activities that provided an intensive 5-week immersion program for diagnosed dyslexic youngsters ages 7-13.

Publications in 2019 (funded wholly or in part with CHECRA funds) not on last report:

Thesis and Dissertations:

Gustafason, K. 2019. Quantifying The Effects Of Residential Infill Redevelopment On Urban Stormwater Quality, M.S. Thesis, Hydrologic Science and Engineering Program, Department of Civil and Environmental Engineering, Colorado School of Mines, Golden CO

Vatankhah, H., 2019, The Role Of Ozonation In Potable Reuse Treatment Trains, Doctoral Dissertation, Department of Civil and Environmental Engineering, Colorado School of Mines, Golden CO

Pfluger, A., 2018. Multiple compartment anaerobic bioreactors for the generation of energy: exploring energy-positive wastewater treatment, Doctoral Dissertation, Department of Civil and Environmental Engineering, Colorado School of Mines, Golden CO

Publications:

Cherry, L., Mollendor, D., Eisenstein W., Hogue, T.S., Peterman, K.u, McCray, J.E., 2019. Predicting parcel-scale redevelopment within the Berkeley Neighborhood in Denver Colorado using linear and logistic regression, Sustainability, 11, 1882; doi:10.3390/su11071882.

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- Panos, C. L., J. M. Wolfand, and T. S. Hogue. (2019). SWMM Sensitivity to LID Siting and Routing Parameters: Implications for Stormwater Regulatory Compliance. *J. Am. Water Resour. Assoc.* In review.
- Pfluger, A., G Vanzin, J Munakata-Marr, L Figueroa, 2018. An anaerobic hybrid bioreactor for biologically enhanced primary treatment of domestic wastewater under low temperatures, *Environmental Science: Water Research & Technology* 4 (11), 1851-1866
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- Pfluger A., J. Starke, S. Cospers, J. Munakata Marr and L. Figueroa (2018). Can Organic Waste Contribute to Energy Security?, *The Military Engineer*, 110 (713), 62-63.
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COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

Appendix F

Raman – SEM/FIB 2020 MRI Update

- (a) A description of the project, the principal persons or entities involved in the project, and the amount of funding allocated to each principal person or entity;

The project consisted of the acquisition of a Raman imaging Scanning Electron Microscope / Focused Ion Beam instrument, the first of its kind in a user facility. This instrument is capable of imaging materials from the millimeter to the nanometer scales, measuring and mapping elemental composition, and identifying and mapping the bonding aspects of the elements such as phases crystal quality, and strain. The focused ion beam can be used for local sectioning to assess these aspects on cross-sectioned faces and for removing identified regions for further detailed analysis by other techniques such as transmission electron microscopy. Additionally the instrument has in-situ heating capability up to 900 °C for evaluating these aspects as a function of temperature. The instrument is open for use on a cost-recovery basis to all academic entities in the state, and at an industrial rate to companies. CHECRA funds were used as partial required cost share in a competitive National Science Foundation (NSF) competition. CHECRA funds in the amount of \$300,000 were used for supporting instrument acquisition. Funds in the amount of \$999,700 were awarded by NSF and used towards instrument acquisition.

Principle Persons:

PI/PD – David R. Diercks, PhD (ddiercks@mines.edu) -no funding support
 CO-PI/PD – Alexis Sitchler, PhD (asitchle@mines.edu) - no funding support
 CO-PI/PD - Melissa D Krebs, PhD (mdkrebs@mines.edu) - no funding support

- (b) The manner in which each principal person or entity applied the funding in connection with the project; and

The CHECRA funds were applied toward the purchase of the instrument. The instrument installation is currently on-going, but the majority of it was completed January 24th, 2020. PI Diercks is taking primary management responsibility of the instrument under the umbrella of Mines' Electron Microscopy Laboratory (EM Lab). Like other EM Lab equipment, this instrument is being ramped up to be supported by cost recovery recharge.

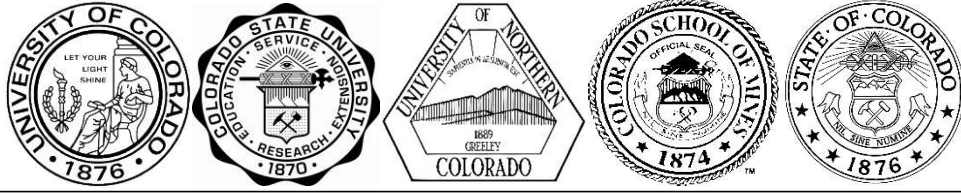
- (c) The results achieved by the project.

With the bulk of the installation just having been completed, there are not substantive results from the instrument to report yet.

However, there are numerous researchers from within several departments at Mines, and from research institutions across the area and the country, including Ohio State University, University of Colorado, the National Renewable Energy Laboratory, United States Geological Survey, and

Pacific Northwest National Laboratory that have expressed specific interest in using this instrument.

The capabilities of this instrument have already be included in an electron and optical microscopy class with inclusion in additional classes planned.



COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

Appendix G

2019 Annual Report for CHECRA matching funds for McKay ARPA-E project

Root genetics in the field to understand drought adaptation and carbon sequestration – PI, Professor John McKay, CSU

ARPA-E ROOTS Award

Colorado State University

CHECRA Grant (\$325.6K over 3 years)

Summary: We are working to develop a high-throughput phenotyping platform to measure root system traits, soil carbon and nutrients, as well as mapping soil surface greenhouse gases (GHG). This platform will be used in field experiments to identify genetic variation in root traits and their effect on soil C stocks and GHG. This understanding will then be used to improve root trait-based model predictions of soil GHG emissions and soil carbon sequestration to depth in an integrated project advancing both trait development and field screening. The project started on 3 July 2017.

Description of the project, the principal persons and the amount of funding:

We will utilize a diverse set of maize lines to examine for root structure and composition under full and limited irrigation in Colorado and Arizona. They will be phenotyped with our existing approaches as well as newly developed root (root pulling force) and soil HTP approaches. The understanding derived from these experiments and the data on root and soil response variables will be used to develop and evaluate a new generation process-based model, to be used to enhance translation and improve throughput of breeding as well as a tool to quantify the impacts of root parameters across ideotypes on soil C sequestration and GHG emissions in different environments. For category 2 we will develop novel sensors, incorporating them into our already functioning field HTP systems. The most promising methods and sensors will be used to identify genomic regions that influence root and soil traits and their sensitivity to drought by screening large mapping populations in the field. Data from this larger field effort will be used to validate the new model. The principal persons involved at Colorado State University are PI John McKay, as well as Co-PIs Francesca Cortufo, Greg Graff, Sangmi Pallickara and Keith Paustian. ARPA-E officials made the decision to terminate task 4, led by Co-PIs Randy Bartels and Thomas Borch, after the task failed to meet milestones.

Funding from CHECRA and allocation:

The CHECRA funds have been used to support PI John McKay, Research Scientist Jack Mullen, and project manager Anne Howard. The CHECRA funds have also enabled purchase of an EarthSense TerraSentia high-throughput phenotyping robot to enhance our field measurement capabilities.

Results Achieved:

Task 1: Technology to Market

M1.4.3 Refined Product Definition / First-Market Fit (Q10)

Present revised product definition in conjunction with Post-project plan to ARPA-E Program Director and T2M Advisor with indicators of potential participation by various stakeholders during site visit on January 16, 2020.

1.4.5 Customer/Partner Engagement (Q4-Q10)

Presented to

- Monsanto
- Indigo
- CIMMYT
- Colorado Corn Growers
- Colorado Governor's Ag Forum
- USDA/DOE Circular Carbon Economy Summit

Conversations ongoing with

- Bill & Melinda Gates Foundation
- CIMMYT
- Corteva

Francesca Cotrufo and Keith Paustian (Tasks 6 & 8)) engaged with Shell.

1.5.2 Update Value model based on industry input (ongoing quarterly)

Developing better sense of value of HTP services, as several partners are beginning to engage on R&D projects to trial. At this point in development, peer reviewed publication is more important than intellectual property protection for generating commercial interest in our technologies and services.

M1.7.2 ARPA-E acceptance of final post-project plan

Present Post-project plan to ARPA-E Program Director and T2M Advisor during site visit on January 16, 2020.

Task 3: HTP platform design and Engineering

There were seven technical milestones due prior to the end of 2019.

- The full RPF instrument was installed on the HTPV and testing was completed fulfilling WBS 3.1.
 - The equipment required to build and validate an RPF sensor (M3.1.1) was tested in Q5.
 - The RPF instrument was installed on the HTPV (M3.1.2) and testing of the system was performed in project Q9.
 - Delivery of the high clearance tractor (M3.1.3) was scheduled to be completed by the end of Project Q4 but due to significant hurdles encountered during the purchasing and manufacturing process, was not delivered until Q6.
- Creation of the soil sampling system (CSS; WBS 3.2) is near complete. The ground penetrating portion of the design has been built and tested on the HTPV.
 - Concept selection for the ground penetrating portion of the soil sampling system (M3.2.1) was completed prior to the end of Q2.
 - Concept selection for the soil sampling system (M3.2.2) has been completed ahead of schedule and was outlined in the Q4 report.
 - Field testing of the ground penetrating portion of the CSS system (M3.2.3) with manual subsampling of the soil core was completed during project Q9.
 - The full subsampling system has been fully designed. The system is designed to be installed on the existing platform and will integrate with the ground penetrating portion of the design.

Field Testing of CSS System.

Construction of the CSS subsystem on the field platform was completed during Q8. As outlined in previous reports, the field-deployed embodiment of the HTPV contains one frame that contains an RPF module and a CSS module. This combined frame is detachable from the HTPV with one mechanical interface and two connection points for all hydraulic power, electrical power, and electrical sensor signals. The field implementation of the CSS system follows the design identified in M3.2.1. A hydraulic cylinder applies a downward force to the top of a coring tube. The force of the hydraulic cylinder is reacted by the tractor through the linear positioning system. The cylinder is outfitted with a ball joint on the top and bottom which allow it to articulate as the tractor moves through the field. The coring tube, however, is attached to the combined frame with two compensated linear bearings that are guided by two vertical rails. These bearings and rails guarantee that the coring tube is driven straight into the ground and any lateral force imparted on the top of the tube by the coring cylinder is absorbed by the combined frame.

Testing of the CSS ground penetrating system were performed with the HTPV stopped in the field. The linear position system was used to move the combined frame along the length of the tractor to the desired coring location. The combined frame was then lowered hydraulically to the ground to allow for RPF testing and coring. Tests were first performed with a custom, Czero-designed coring tube to core to a depth of roughly 0.95 meters. Because required coring forces were unknown leading into the design of the system, Czero determined that a modified version of a Commercial Off the Shelf (COTS) coring cylinder should be designed and built. The modified design has sampling holes drilled through one side of the cylinder every 10cm. The design is slightly longer than the COTS version and has a higher wall thickness as well. The increased wall thickness was added to prevent buckling in the case of high required driving force. During testing, the coring tube was driven into the ground via the telescoping hydraulic cylinder. The coring cylinder had no issues driving the coring tube into the ground at maximum

depth. The cylinder was able to retract the coring tube from the ground but required higher supply pressure as compared to the coring operation.

After retracting the coring tube from the soil, it was apparent that the modified tube design was not a viable option, largely due to the expansive nature of the soil at the test facility. Upon initially entering the tube, the soil expanded and created a blockage in the lower 0.2 meters of the tube. Once the blockage was present in the end of the coring tube, the CSS system continued to compact soil into the hole as it continued downward.

After the first round of CSS testing was completed, a COTS soil coring tube was modified to replace the custom tube. The COTS version was slightly shorter than the custom tube, had a smaller wall thickness and therefore larger inside diameter, and had a lengthwise slot machined along the tube that could be used for sub sampling. Because of the relatively low force required to drive the coring tube in the first round of testing, concerns about buckling of the tube during coring were eliminated.

Testing with the COTS tube went as expected. The CSS system was able to drive the coring tube into the ground at full depth (~0.85 meters) and was able to retract the tube. After the tube was retracted, it was removed from the CSS system and manually subsampled every ten centimeters. This process was repeated, and sub-samples of the core were taken for three different cores. We analyzed nitrate concentrations from these soil subsamples, which showed that we can observe differences in nutrient levels with soil depth with this coring setup (Fig. 3.2).

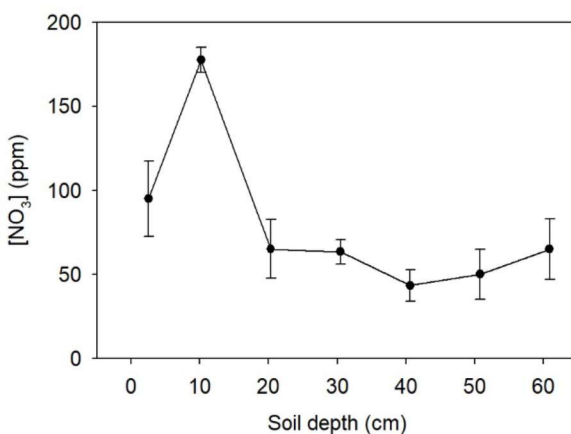


Figure 3.2. Variation in nitrate concentration with soil depth (mean \pm SE, $n = 2-3$).



Figure 3.1. COTS coring tube containing soil core.

Task 5: Field plantings and phenotyping

M5.2.3 Initial analysis of plant phenotype data.

We completed our main phenotyping including RPF measurements at two developmental stages during Q9, and we processed root systems from our RPF measurements for imaging and root-mass ratio estimates and harvested plots in Q10. The root systems have been sent to the Danforth Center for X-ray CT. Initial analyses of RPF showed significant genotype effects in all times and treatments, with heritabilities ranging from 51% to 59% in the wet treatment and 38% to 47% in the dry. Therefore, we have conducted GWAS on both root and shoot traits from 2018 and 2019 field seasons, and have identified several interesting candidate SNPs for further study (e.g., Fig. 5.1). Some of the significant SNPs for RPF are also significant when looking at root imaging traits such as root area and width, suggesting a basis for the differences in RPF. For one of our larger effect RPF QTLs, SNP_8, the alternate alleles showed a constitutive difference across our sites and treatments (Fig. 5.2).

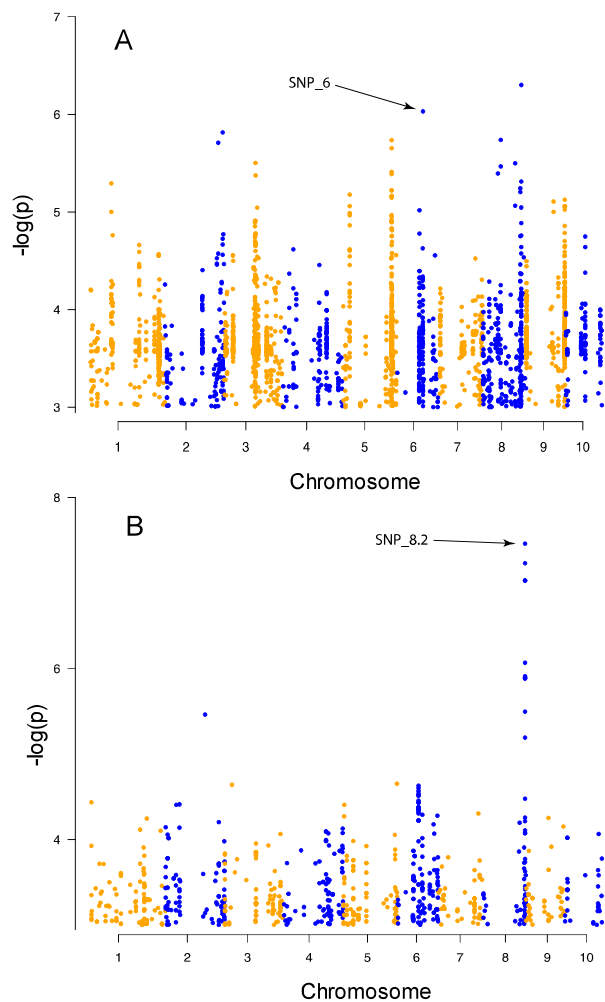


Fig. 5.1. Sample GWAS Manhattan plots for RPF for (A) dry and (B) wet treatments from 2018, identifying significant SNPs.

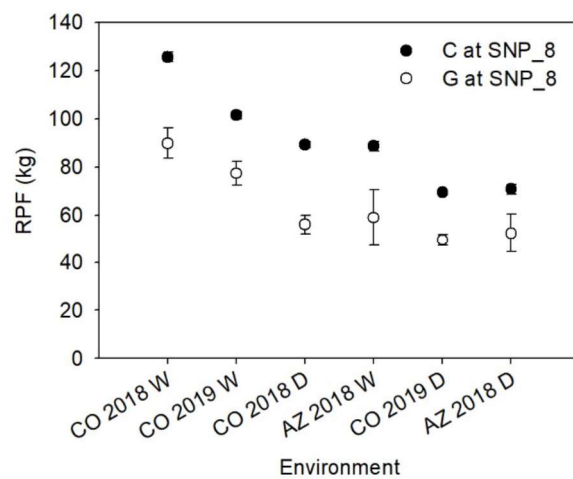


Fig. 5.2. Allele effects of SNP_8 on RPF across sites and treatments (mean \pm SE). Environments are sorted from least to most stressful.

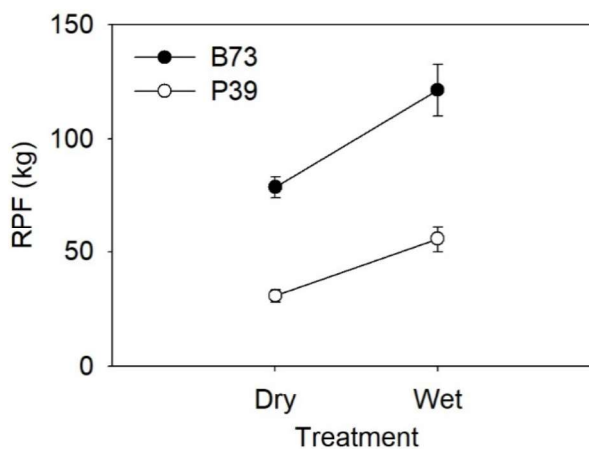


Fig. 5.3. Differences in RPF in the RIL mapping population parents B73 and P39 (mean \pm SE, $n = 2$).

Preparations for 2020 field season.

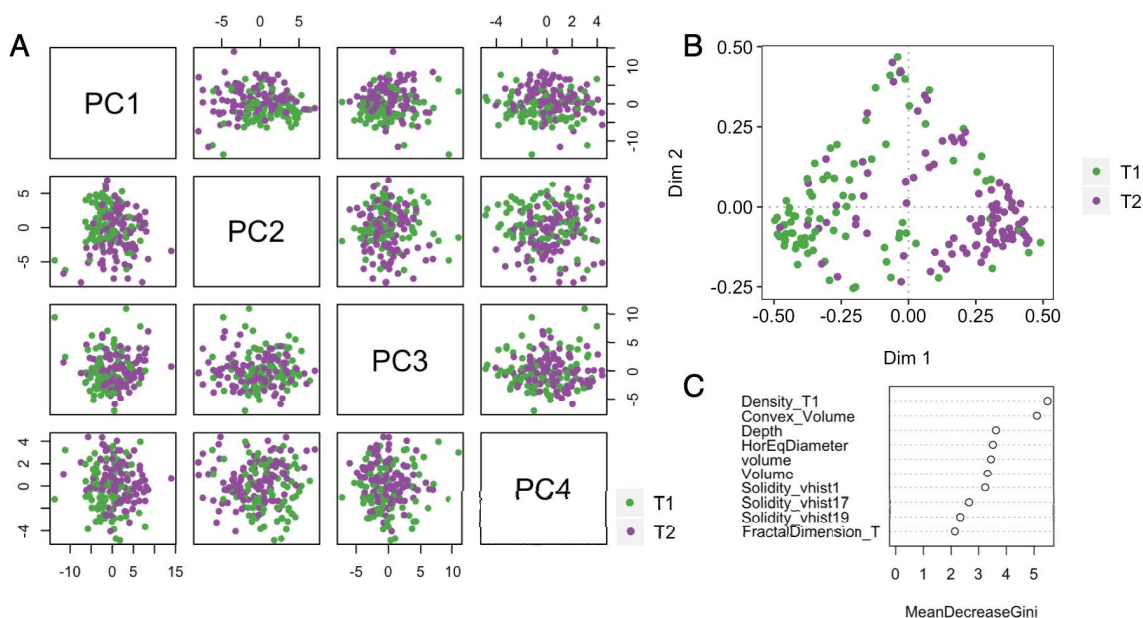
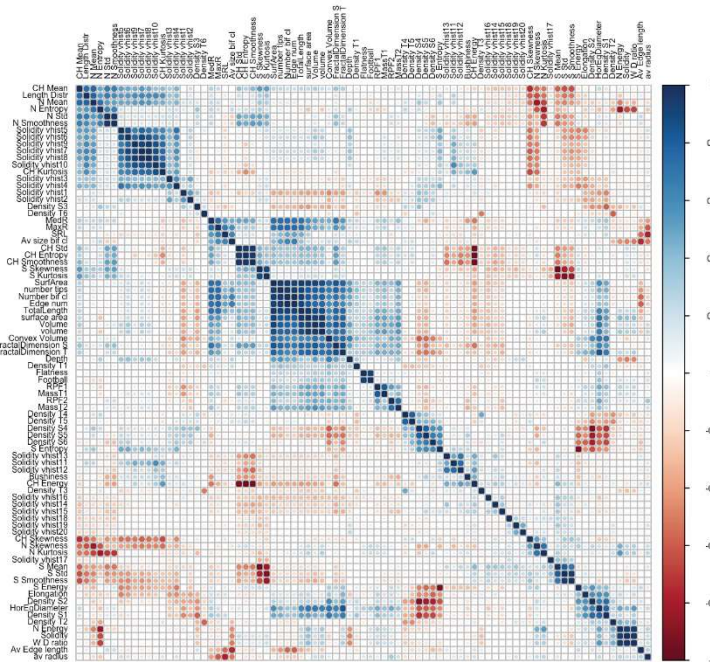
We plan to grow and phenotype multiple NAM RIL populations from bi-parental crosses to estimate effect size of GWAS hits in 2020. We are currently selfing RILs in the greenhouse for

two mapping populations to bulk seed for the field at CSU, and we have 6 populations growing in the field in Mexico to bulk seed as well. These populations show variation in root traits (Fig. 5.3), and also vary in alleles at significant SNPs (e.g. those of Fig. 5.1).

We are also planning a field experiment on nitrogen-use efficiency and changes in root traits in Pioneer ERA hybrids, in collaboration with Corteva. We will measure grain yield increase at same fertility, and use time series sampling of soil, as well as root and shoot traits to look at N budget over the season.

M5.4.2 3D phenotypes of excavated root systems.

In fulfillment of this milestone (3D root architecture analysis of 144+ samples), from two field seasons the Topp Lab has to-date performed X-ray computed tomography and 3D phenotypic trait extraction from a total of 286 pulled root crowns. We are also now beginning phenotyping of 2019 root systems. From the 2018 field season, 20 genotypes of the maize SAM panel from 2 treatments and 2 time points were X-ray imaged, for a total of 270 root samples scanned. From this, the measurement of 3D traits from 202 samples has been fully completed.



Within the 202 finished samples from 2018, RPF earlier in the season is most significantly

Figure 5.5. (A) Principal component analysis from 3D architecture traits of the 2018 field roots, colored by time point. (B) Random forest could distinguish between time point 1 and time point 2 root samples using 3D phenotypes at an accuracy of 78% (leave-one-out cross validation). (C) The most important traits for distinguishing time point 1 vs time point 2 were related to density, volume, depth, network width, and solidity.

positively-correlated with root surface area, volume, network width, and root complexity (Figure 5.4). These traits are largely also the most significantly positively-correlated traits with root pulling force later in the season. Principal component analysis also shows good distinction between samples based on time point (Figure 5.5A). Likewise, random forest classification was more accurate for time point (Figure 5.5B) than for treatment, although distinguishing by both time point and treatment together may be more informative and result in higher accuracy. Interestingly, the root traits most important towards random forest classification were different for time point (Figure 5.5C) than they were for treatment (not shown), suggesting that the latter does not simply affect phenotype in a manner akin to delayed development.

Task 6: Experimentally quantify root contributions to C and N stocks in Agricultural soils

In May 2018, we established the root tissues and exudates field incubation at the ARDEC, as reported in previous reports. The experiment was a randomized design with 5 input treatments (Z013root, Z022root, Z013exudate, Z022exudate and no-input control), 3 depths (0-20, 20-50, 50-90cm) for the root input and one (0-20cm) for the exudate input, 4 total harvest times, in 4 replicate blocks. For the first two harvests root exudates and control cores were removed and the maize plant adjacent to each harvested core was also sampled. For the third harvest root exudates, root biomass, and control cores were removed and the maize plants adjacent to each harvested core were also sampled. For the fourth harvest no maize plants were collected, since it coincided with the beginning of the growing season. Maize biomass was measured at the first three harvests and %N and $\delta^{15}\text{N}$ were measured on biomass samples to determine if the maize plants had taken up any ^{15}N derived from the exudate input. Harvested cores were split by depth- 0-20 cm, 20-50 cm, and 50-90cm using a circular saw and kept cool while processing. All of the soil from all four harvests were 8 mm sieved, with a subsample 2 mm sieved. One subsample of the 2mm sieves soil was finely ground and oven dried for elemental and isotopic analyses, while another was stored at $-80\text{ }^{\circ}\text{C}$ for potential future microbial work. All of the soils from all four harvests were fractionated into dissolved organic matter (DOM), light (Light POM), and heavy particulate organic matter (Heavy POM), and silt and clay size mineral associated organic matter (MAOM) fraction.

The bulk soils, fractions, and the aboveground plant biomass from the first three harvests have already been measured on an isotope ratio mass spectrometer for C and N concentration and ^{13}C and ^{15}N enrichment, at the EcoCore analytical facility. The belowground biomass, soils, and soil fractions from the fourth harvest are currently being run on the isotope ratio mass spectrometer.

After one year in the field, we found that about 20% of the C and over 50% of the N entering the soil through root exudates remain in the soil, largely stabilized through mineral association (Fig. 6.1). Contrary to our hypothesis, despite the differences in litter chemistry (see previous reports) there were similar amounts of C and N remaining in the soils from the root exudate of the two maize varieties (Fig.6.1). Exudates were incubated in the 0-20cm, and only negligible amounts moved below the depth of incubation. There were small amounts of exudate C found at the 20-50 cm depth. For the exudate N, small amounts were found at the 20-50 cm and 50-90 cm (Fig. 6.1), indicating that root exudates mostly contribute to the formation of organic matter in the depth layer where they are exuded.

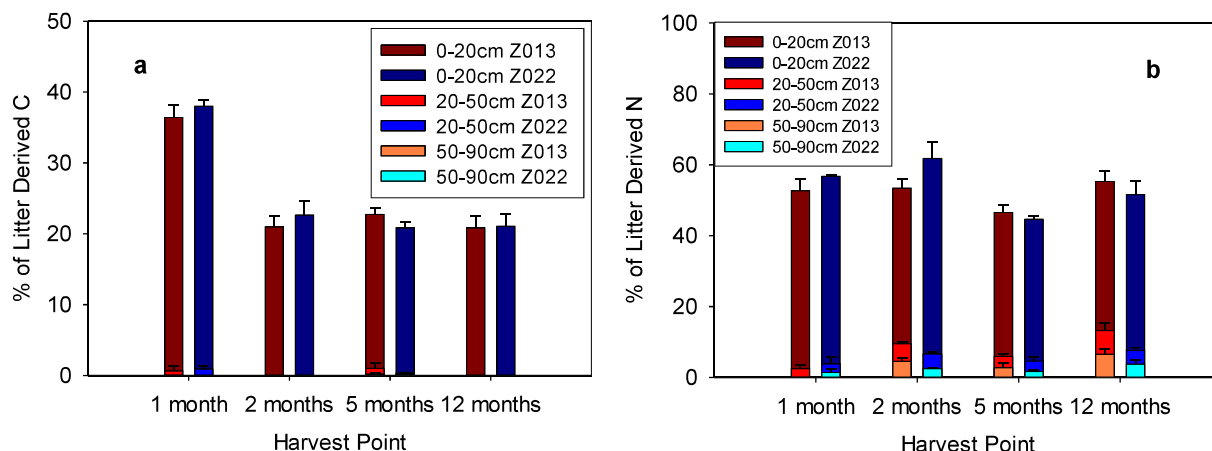


Figure 6.1. Exudate-derived C (a) and N (b) remaining in the soil at different depths at the four harvest points from the two maize varieties added in the 0-20cm depth.

We found the majority of the root-exudate derived C in the mineral associated organic matter (MAOM) (Fig.6.2). Although we did not see differences between the two corn varieties when looking at the whole soil we found variety differences when comparing the soil fractions. As hypothesized, the Z22 variety, which has lower C:N, had greater amounts of litter derived C in the MAOM fraction in the first two harvests, but that difference was gone by the 5 month harvest.

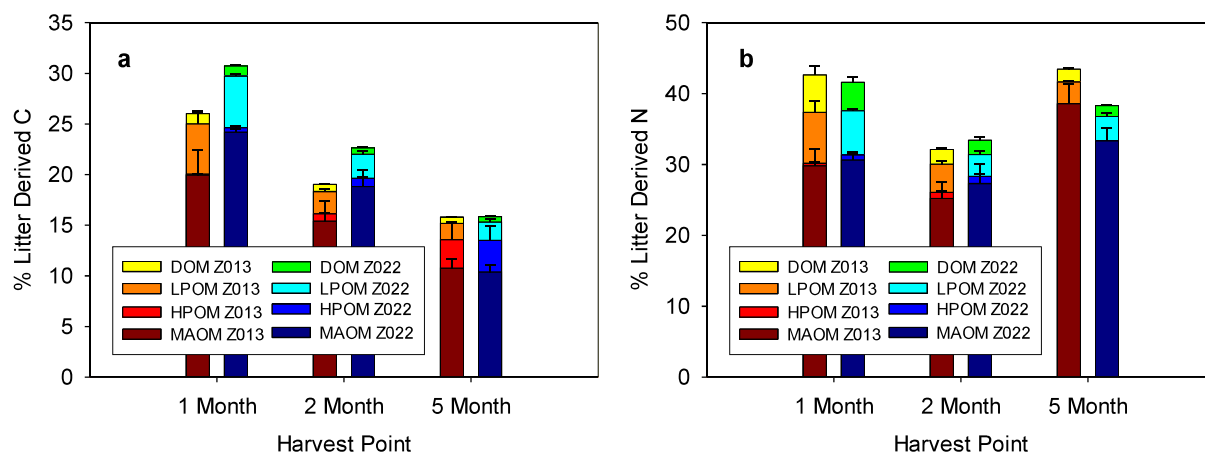


Figure 6.2. Exudate-derived C (a) and N (b) remaining in the different soil fractions in the 0-20cm depth at the four harvest points from the two maize varieties.

Regarding the labelled root tissues, at the five-month harvest the majority of the added root litter had been decomposed with only 4-7% of the root C remaining in root residues in the 0-20 and 20-50 cm depths, and 12-16 % in the 50-90 cm depth. Thus, despite decomposition progressing quickly during the summer months in this irrigated corn field, relatively slower rates were measured at the deeper (50-90 cm) depth. The Z22 variety had slightly less decomposition at the 50-90cm depth compared to Z13. There were even lower amounts of root N remaining as compared to C, possibly due to N mining. As the root tissues decomposed, the majority of the root-derived C and N was found in the light particulate organic matter (LPOM)

at the 5 month harvest (Fig.6.3). There was less litter derived C and N at the 0-20cm depth, as compared to the other depths. There was also a large difference between the amount of litter derived C and N between the two corn varieties with the Z22 variety having less litter derived C and N in the POM fractions, indicating faster decay of this more labile litter.

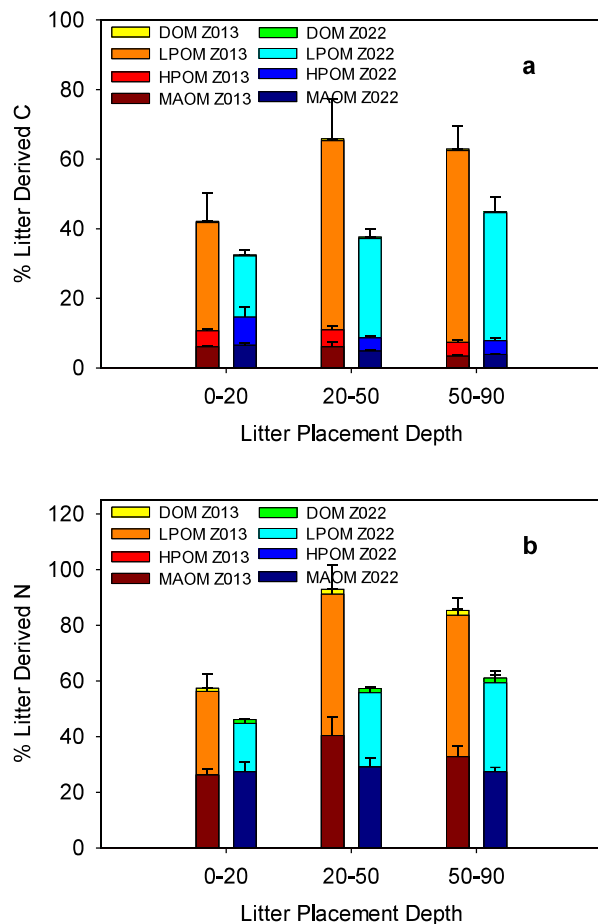


Figure 6.3. Root-derived C (left panel) and N (right panel) remaining in the soil fractions at the different placement depths at the five month harvest point from the two maize varieties.

Overall our data support the idea that root exudates and the water-soluble components of root tissues contribute to MAOM formation, while root residue decomposition contribute to the formation of POM. The two-year harvest results will allow us to assess the persistence and efficiency of these processes.

Task 7: Data management, analysis, and visualization

M7.2.1 Prototype Radix with visual analytics features

Analytical features. Our front-end dashboard is capable of providing visualization over the underlying plot data – currently, we support heatmaps over a user-selected polygon and single-plot analytics over time. The access to the dashboard is restricted to users with proper credentials. Users can create their own set of spatial polygons over the plots for reuse later.

Figure 7.1 shows a snapshot of the dashboard over the sensor data collected from Maricopa, AZ fields.

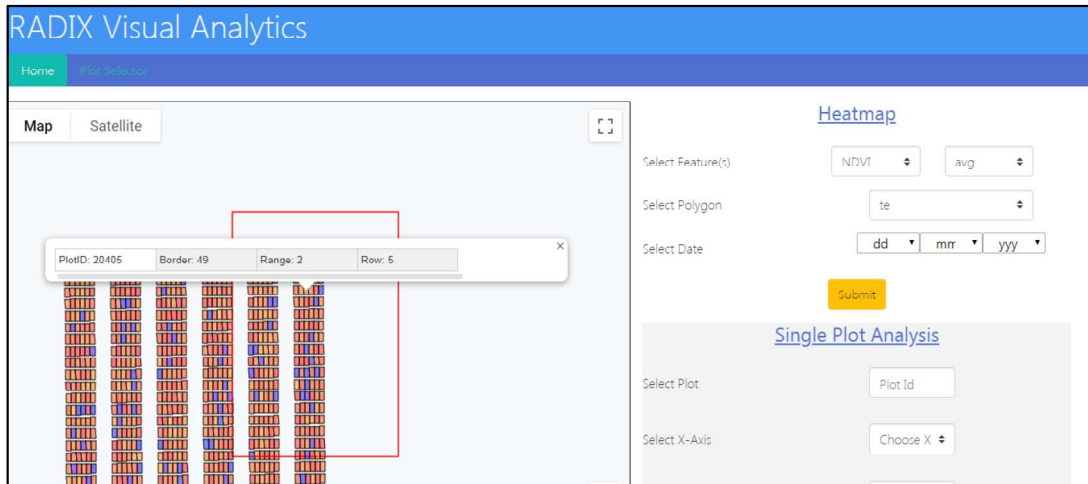


Fig. 7.1. Visualization of plot data at the front-end.

Missing Data and Irregular Measurements. Due to the varying nature of individual sensors and how they collect their data, we have pre-processed the readings to adjust to the actual positions of the sensors with respect to the GPS antenna that records the position of the recording. Also due to the method of data collection for various sensors, the sensor data in some cases needed correction based on the position of the sensor at a current instance – for instance, the angle of sweep of a LIDAR sensor at a particular instant. Thus, in case of Arizona, against each individual GPS coordinate, we have only a single sensor reading. So, each sensor data is processed, geo-located and grouped separately for each plot. This allows visualization queries over particular sensors easier to decipher. We have now automated the entire process of pre-processing and insertion of new data into the RADIX/IRODS storage system.

Data Archival and Retrieval with CyVerse. Along with geo-tagging and storage of plot data on the RADIX back-end, a permanent copy of the data-blocks are also maintained in IRODS. The offloading of freshly inserted plot data into IRODS is done periodically at a pre-configured interval of inactivity after every new data dump into RADIX is completed. The permanent IRODS copy of plot data can be fetched by any user wanting to work with raw sensor data for a given plot(s). Along with the ability to fetch the data blocks, we also provide an inbuilt data-integrity check for the downloaded components.

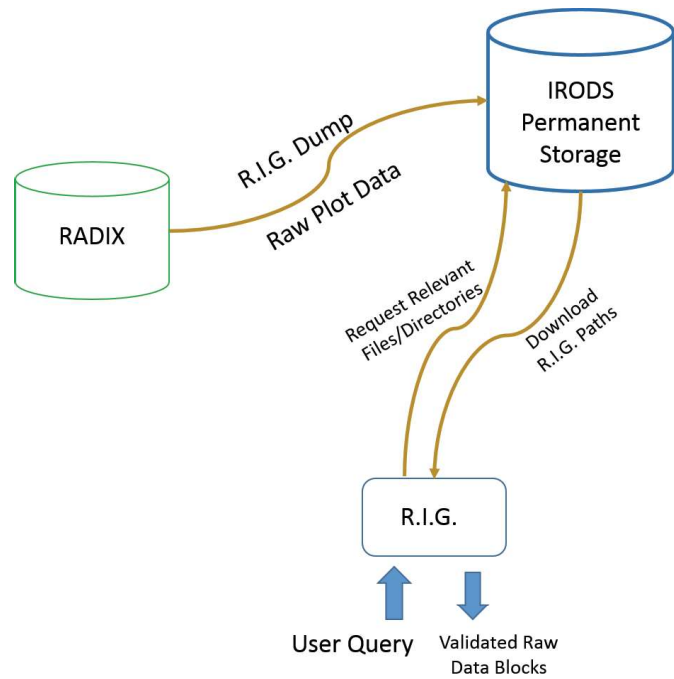


Fig 7.2. Breakdown of R.I.G. initialization, querying and download with integrity test.

Since the IRODS system contains no partitioning information for the data files, we need to rely on some external metadata to determine which data blocks inside IRODS is relevant to a user query (which might specify a geospatial polygon and a time-range as its constraints). We need a map between the IRODS data files to the actual spatiotemporal and other sensor-related features they represent. For that purpose, we have implemented the RADIX Integrity Graph (R.I.G.), a hierarchical feature graph that maintains both metadata and checksum information for the hierarchical directory structure at IRODS (as shown in Fig. 7.2).

R.I.G. Initialization. Any individual node can be a R.I.G. server by initializing the R.I.G. using the R.I.G. dump. During the periodic offloading of plot data into IRODS, RADIX also dumps metadata related to the files being offloaded along with the checksum for each of those individual uploaded files – this is what we call a R.I.G. dump.

During its startup, the R.I.G. server fetches these dump from IRODS to generate the R.I.G graph, a feature graph, similar to the in-memory metadata graph in RADIX, where each node maintains two kinds of information – a) the feature metadata of the directory it represents and b) the checksum of that directory, generated in a bottom up fashion.

Locating Raw Plot Data from IRODS. Users trying to fetch raw plot data from IRODS can query the R.I.G. server, which acts a middleware/mapper between the user query and the files in IRODS. It is to be noted that the directory structure at IRODS mirrors that used internally in RADIX. Using the R.I.G. feature graph, we can figure out which path(s) in the graph satisfy the user query. The leaf node of each path can either be a directory in IRODS or a file. R.I.G. requests the paths/directories corresponding to the matching nodes, thus reducing the number of file downloads from IRODS.

Integrity test of downloaded components. As previously noted, the R.I.G. nodes contain checksum information for the directory/file they represent. If the path being requested from IRODS is a file, the checksum of the file can be compared to the checksum of the node to check for integrity. In case the download is for a directory, the checksum of the directory is generated in a hierarchical fashion from the directory tree inside that directory to get the checksum of the root for comparison. Fig. 3 shows a breakdown of the R.I.G. initialization and request operations.

Updating the Hash-grid

An issue we also looked into for this quarter was to work on updating our geohash-based hash-grid to fix the corner-case scenario where all plots in a field might not share a common geohash. The hash-grid is used to geo-locate sensor data to the actual plot to which they belong. Currently, the hash-grid implementation makes the assumption that all plots in a field share a single base geohash, and assigns identifies smaller grid boxes inside with respect to the containing geohash.

We have updated the hashgrid implementation to allow the more

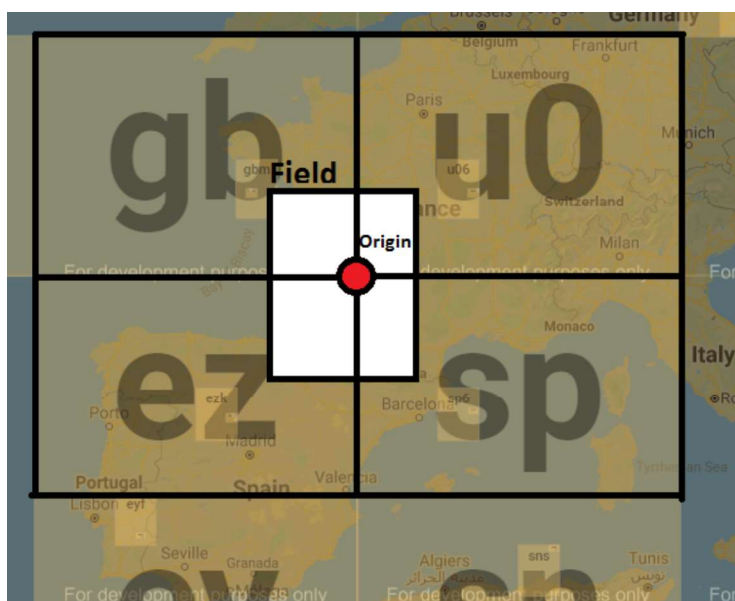


Fig 7.3. Field lying between 4 unique geohash boxes.

generalized case of plots in a field spanning up to 4 unique geohash boxes and using the common point between the geohash boxes as origin and then providing the grid Id based on that origin.

Fig.7.3 shows a sample scenario where a field may straddle 4 unique containing geohash boxes. In such a scenario, the common point between the 4 bounding geohash polygon acts as the origin w.r.t. which we generate unique identifiers for each smaller geohash grids.

Storage of Sensor Data Summary from Arizona Plots

Along with storing of raw data, the RADIX distributed system maintains in-memory summary data against each plot in a hierarchical metadata graph which assists in fast identification and retrieval of summary data against each plot along with the block pointers to the data for that plot. This in-memory summary graph speeds up the generation of visualizations such as heatmaps much faster.

Finalizing the coordination between the back-end storage and the front-end visualization components

We have set up the front-end visualization interface to interact with the back-end storage to query and load visualization requests and responses respectively. Fig. 7.1 shows a snapshot of the interface displaying heatmap results of the plots lying within a given polygon for a specified time. Per-plot analysis/ comparison is also available but will make more sense once data from more dates are incorporated into the back-end storage. Also, we are currently in the process of setting up documentation in the front-end web page to contain tutorials and instructions on download, deployment and usage of the various RADIX components.

M7.4.1 Genotype/environment root effects.

We have further investigated 3 root QTL identified in Task 5. We fit a poly-qt1 anova to examine effect sizes of the three loci (Fig. 7.4). SNP_8 was a mid-sized effect QTL and had the largest effect at the end of season, while the effect of SNP_6 was more prominent at mid-season. SNP_8 is also of interest due to its constitutive effect across sites and treatments (see Task 5), making it likely to be more broadly applicable. The genes in which these SNPs are located are consistent with the observed phenotypes.

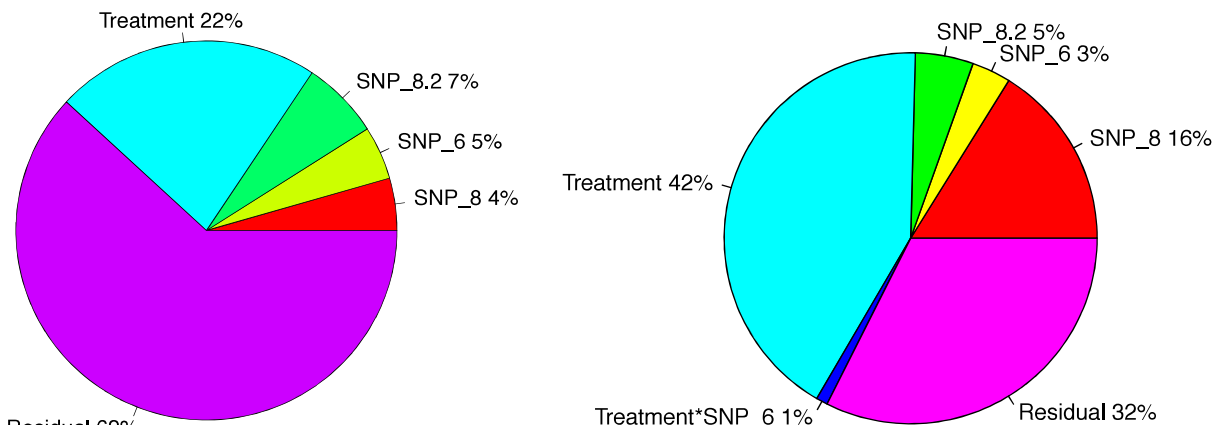


Fig. 7.4. Effect sizes of 3 SNPs of interest based on multi-qtL anova.

Task 8: Modeling of soil C and N dynamics

In this quarter, we improved the annual crop simulation submodel we added into the model in the previous quarter. Improvements included simplification of the gross primary production method (but achieving similar accuracy), we used a new method for leaf senescence, and added user inputs to control biomass allocation between aboveground and belowground. We also modified the annual crop submodel to be able to simulate perennial crops.

The SOM decomposition submodel was slightly changed as we found the old method did not produce accurate results for SOM carbon to nitrogen ratio. The new method is shown in Figure 8.1. We coded a management practices template to let the user schedule management operations (not finished yet). Some bug fixes were conducted in our testing. Some new simulation results illustrating the performance of the crop submodel are shown below.

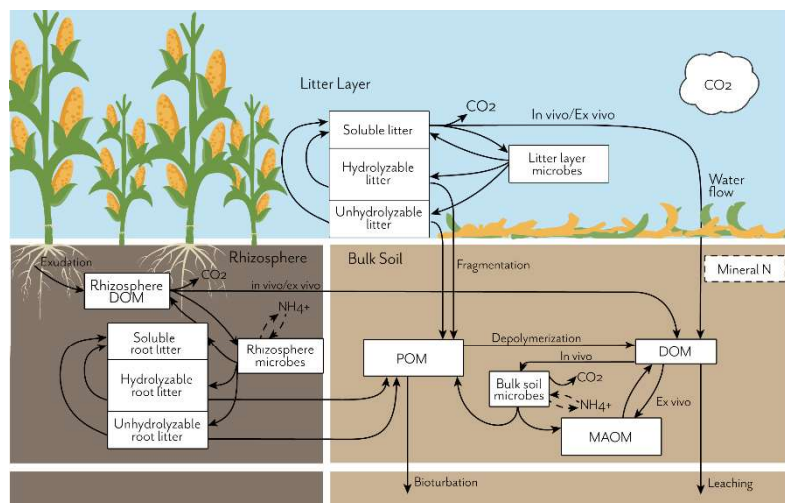


Figure 8.1. Schematic representation of the plant litter and soil organic matter components of the MEMS v2 ecosystem model. The full model represents C and N fluxes among atmosphere, plants and soil, into multiple layer down to a user defined depth. Inputs and recycling of N causes feedbacks to NPP which is allocated above or below-ground and at different depths, depending on vegetation/soil traits. Plant C and N inputs (simulated in the plant growth submodel) are allocated to three different measurable detritus pools that differ in their solubility and chemical structure. Root exudates contribute to the rhizosphere DOM pool. These plant

input pools decompose through leaching, microbial catabolism/anabolism and fragmentation, with different rates depending on the pool C:N chemistry, temperature sensitivity, and mineral N and water demand/availability. Microbial and plants debris contribute to three physically defined and measurable soil organic matter pools, according to the current state-of-the-science (e.g. the dual-pathway model of SOM formation (Cotrufo et al. 2015), in-vivo versus ex-vivo microbial processing (Liang et al. 2017) and point-of-entry (Sokol et al. 2019)). Microbial pools immobilize and mineralize N, which feeds back to plant production and soil biogeochemical processes. Multiple soil layers are represented, with DOM and mineral N moving along the soil profile and roots contributing fresh inputs at depth.

Simulation Exercise 1 -- a continuous corn site in Eastern Nebraska.

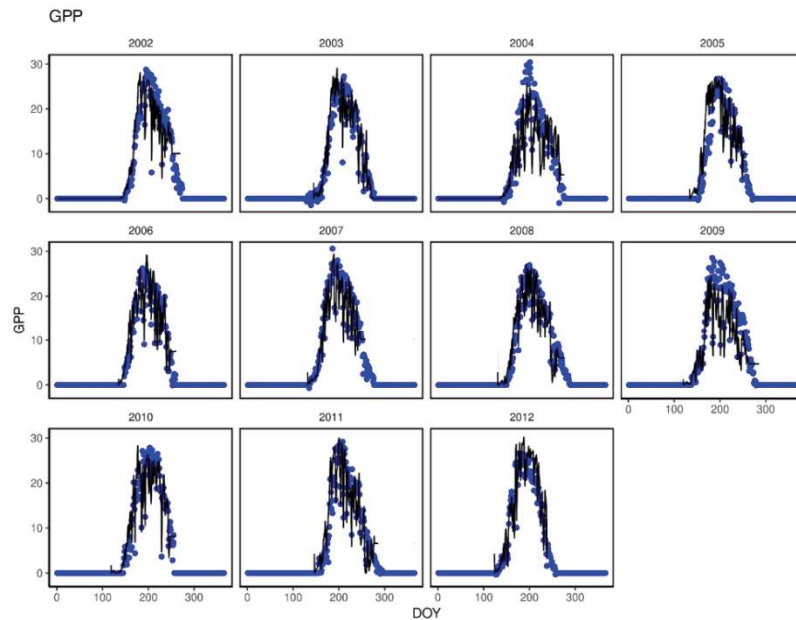


Figure 8.2. Comparison of measured (blue dots) and simulated (black lines) daily gross primary production (GPP).

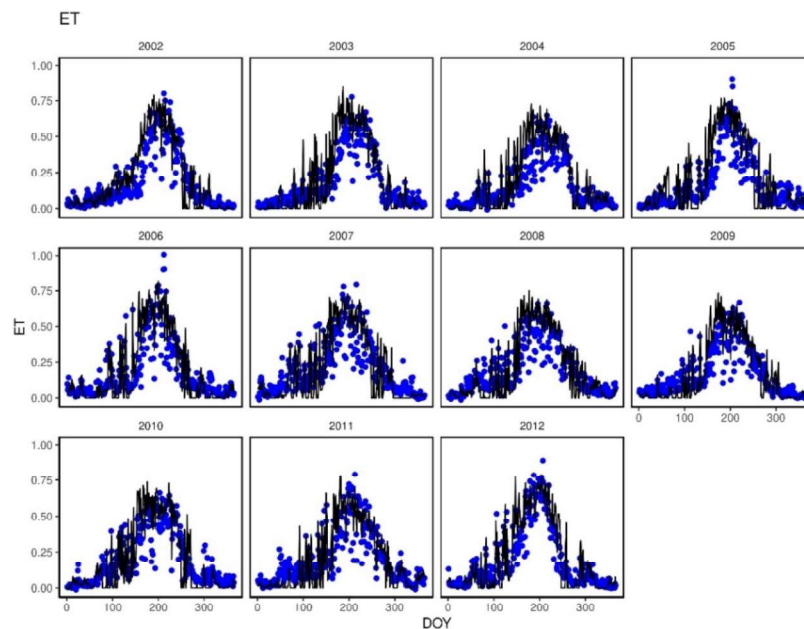
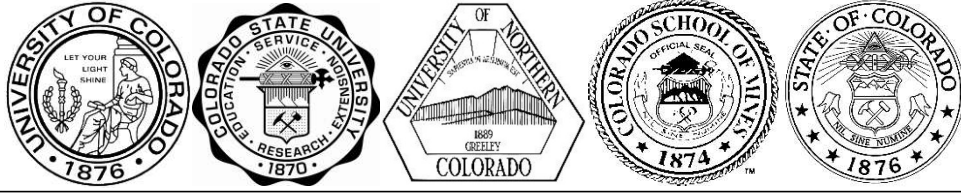


Figure 8.3. Comparison of measured (blue dots) and simulated (black lines) evapotranspiration (ET).



COLORADO HIGHER EDUCATION COMPETITIVE RESEARCH AUTHORITY

University of Colorado:Colorado State University:University of Northern Colorado:Colorado Schools of Mines:State of Colorado

Appendix H

MRI: Acquisition of a Maskless Lithography System**NSF-MRI Award # 1727044****PI Kristen Buchanan****Co-PIs Stuart Field and Mingzhong Wu****Department of Physics, Colorado State University****Project period: 09/15/2017 - 08/31/2020****CHECRA Grant (\$66,482 over 3 years)****Date of report: February 25, 2020**

Summary: This award is an instrumentation award that has enabled the acquisition of a maskless lithography system at Colorado State University (CSU). Photolithography is a critical capability for nanoscale and materials science and this award has allowed CSU to acquire a maskless lithography system that is enabling a wide range of nanoscience-related research at CSU and at neighboring institutions in the Northern Colorado/Wyoming area. The instrument has a high resolution, determined to be 0.6 microns upon installation, and the ability to easily align to pre-existing patterns. This tool is optimized for the direct writing of lithographic patterns over a small area and is well suited to a research environment where the ability to easily reimagine and redesign a sample is a particular asset. The new maskless lithography system is being used for a variety of research projects including studies of spin dynamics in magnetic nanostructures, superconducting vortices in films with micron-scale features, and novel spintronic devices. Other projects that will benefit from this new capability will use the tool to add electrical contacts to ZnO nanorods, to create novel micron-sized biosensors on silicon and glass, to fabricate nanostructures that have unique properties of wettability, and to make high-efficiency solar cells. The instrument is being operated as a user-accessible tool and is available to any interested users. It will enable new research and will be directly benefit students. Since there are more than 28 research groups in the northern Colorado/Wyoming region that have a need for this instrument we expect that our already robust user base will continue to grow.

Funding from CHECRA and allocation: The CHECRA funds have been used to support the mandatory cost share for an NSF-MRI proposal. The NSF provided \$212,031 towards the purchase of a maskless lithography system; the CHECRA funds (**\$66,482**) were used in part towards the purchase of the instrument, and then the remainder is being used to support graduate students who are developing training materials and a web site to advertise the tool, maintaining the instrument, and training users.

Major Activities: CSU acquired a maskless lithography system , the LW405C laser writer produced by Microtech s.r.l. of Italy, using funds from the NSF MRI award and CHECRA, and the system was installed in April 2018. Since the installation, we have developed a healthy user base for the instrument. Thus far 42 users have been trained and the instrument is well utilized. As of 8/2019, the instrument was used for 110 out of a total of 127 of the business days that it was open for users between installation and 8/2019, and the utilization since then has been steady. Several days have been taken up for upkeep and maintenance, but the instrument down time has been only a few days since installation. Some users are able to pattern samples within an hour or two so there is still capacity in the schedule to accommodate new users and users, once they are sufficiently trained, are allowed to use the instrument after hours. Our instrument oversight committee will be consulted if any issues arise with user scheduling but thus far this has not been necessary. This instrument significantly enhances CSU's photolithography capabilities. It is being

used by students and researchers from three colleges at CSU and is attracting widespread interest from not just researchers at CSU but also from other institutions in Colorado and Wyoming, and visitors/collaborators.

Two graduate students have been hired using the CHECRA funds to maintain the instrument and train users over the past year. The students have worked on further development of the web site and training materials for the instrument, have trained new students on the instrument, and oversaw the maintenance of the instrument. Our technician from the summer of 2018, Gus DeMann, stayed on through the spring of 2019 as the main point of contact for training and maintenance. Several minor issues with the operation were identified and Gus worked with the instrument manufacturer to troubleshoot the problems to ensure that the users could successfully make samples. In the spring of 2019, we hired a new graduate student, Weston Maughan, part time to share these duties so that Gus could train Weston. Gus graduated with his PhD at the start of the summer of 2019 and Weston took over the management of the instrument and user training for the summer. Gus and Weston both have extensive photolithography experience, and the model we are currently using where we have graduate students, overseen by the PIs, as the primary trainers, is working well for the management of this instrument.

During the first project year we launched a web site for the instrument:

<http://physlabs.colostate.edu/lithography/>

and the web site and training materials for the instrument have been updated over the past year as new training materials have been developed. The web site includes information on the instrument capabilities, examples, and it explains how to gain access to the instrument.

Thus far 42 users have been trained, where 35 of these are students. The remainder are faculty and research associates. Seven of the users are from outside institutions, where five are from Colorado School of Mines (Singh and Eley groups), one is from the University of Denver (Zink group), and one is from the group of a former CSU graduate student and continued collaborator who is now faculty at Georgia Southern University. We also expect additional new users from outside institutions in the coming project year, e.g., from Xin Fan's group at the University of Denver, and, based on the large number of faculty and students who have expressed interest in this tool from CSU and the surrounding area, we anticipate that the user base will continue to grow.

Nine of the students who have used the instrument thus far are undergraduates, eleven of the trained users are women, and four of the nine undergraduate students are women. Rachel Tenney, a participant in the NSF-funded Research Experience for Undergraduate Program hosted by CSU's Chemistry Department who worked with PI Buchanan last summer won an award for her poster presentation on her summer research project at the APS four corners conference last fall. An undergraduate student from Georgia Southern University, Aron Guerrero, is a McNair Scholar and he spent a week at CSU working with PI Buchanan's group making samples for an experiment on spin waves. Georgia Southern does not have lithography facilities, so access to this instrument allowed him to learn important skills, and to spend time interacting with graduate students in a research setting, both of which will help him to prepare for graduate school. Collaborations like this are valuable not just scientifically but also for graduate student recruitment into our programs at CSU. Co-PI Field is also working with two CSU undergraduate students on projects related to superconductivity that utilize the laser writer. All of the trained students, graduate and

undergraduate, are acquiring valuable photolithography skills that will translate well to future research endeavors in academia or in industry.

The two graduate students who have assisted with training users and maintaining the instrument, Gus DeMann and Weston Maughan, have also benefited from both of these experiences. Gus defended his PhD this summer and moved on to a job with an instrument manufacturer, Stanford Research Systems. His intimate knowledge of the inner workings of the lithography system and his interactions with users were valuable training experiences for his new job.

In the coming year, we plan to continue to train users and to use the instrument to pursue research in magnetism, spintronics, superconductivity, and related areas. We will continue to develop training materials including standard procedures for patterning the most common photoresists, and we will advertise the instrument broadly to the CSU and Colorado/Wyoming research communities to develop a broad user base and to ensure that as many research groups and students as possible have the opportunity to benefit from the instrument. We also intend to use the developed training materials to create a short course to teach students about photolithography techniques and will advertise this to CSU students and to students at neighboring institutions. Since this is the last year of this project, we will consult with the instrument oversight committee to develop a plan for instrument oversight and fee structure that will keep the instrument operational and accessible in future years.

Benefits that the project has brought to Colorado: The CHECRA funds were used to support the purchase of the instrument and the salaries for graduate students who are training new users. The students are benefitting directly from the opportunity to improve their photolithography and teaching skills, and the instrument significantly enhances CSU's photolithography capabilities. The instrument is being used by students and researchers from three colleges at CSU and is attracting widespread interest from not just researchers at CSU but also from other institutions in Colorado and Wyoming. Many cutting-edge areas of research in physics, engineering, chemistry, and biology depend on the ability to make structures with sizes of a micron or less. This instrument is being used for research that is relevant to technology, especially solid-state electronics including magnetoelectronic (spintronics) devices, and biomedical research that are beneficial to society. Because the instrument has a user base with such broad interests, we anticipate that it will facilitate interactions between user groups and new cross-disciplinary scientific collaborations. It will also help to broaden interactions with local companies. One of the participants in the initial training seminar was from Broadcom's Fort Collins location, a company that has an active interest in micro and nanofabrication. A total of 28 research groups have been identified as potential users. Most are from Colorado State University from the Departments of Physics, Electrical Engineering, Chemistry, Biological Sciences, Chemical and Biological Engineering, and Mechanical Engineering. One is a local company (Broadcom). We also have users from Colorado School of Mines (M. Singh's group, and Serena Eley) and the University of Denver (B. Zink's group) and new inquiries from researchers at the University of Denver and the University of Wyoming. Based on the large number of faculty and students who have expressed interest in this tool from CSU and the surrounding area, we anticipate that the user base we already have (42 trained users) will continue to grow. This instrument is being used to teach a broad range of undergraduate and graduate students and postdocs photolithography skills that will translate well to a variety of research areas in academia, government research labs, and industry. The PIs are also giving tours to student groups like the Society of Physics Students.

The instrument is being used frequently for projects in nanomagnetism and spintronics, superconductivity, and drug uptake studies. Some examples of some of the work that has been done thus far are shown in the Figs. 1-8 below.

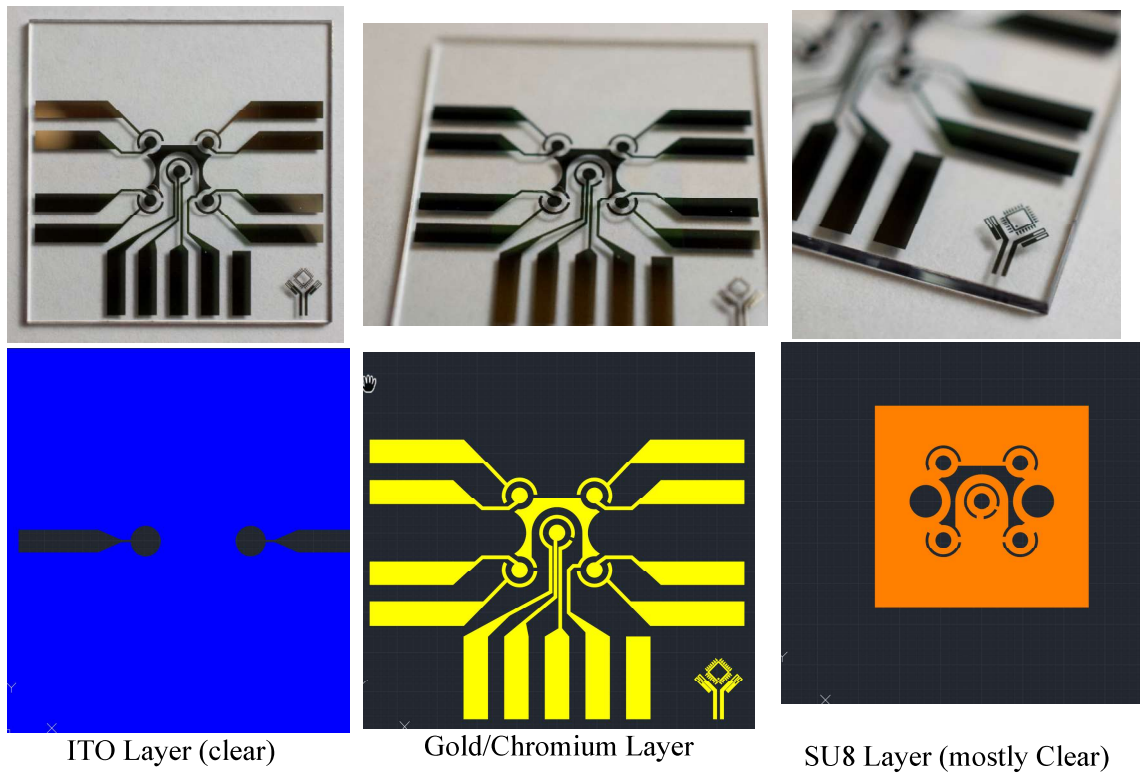


Fig. 1: Biomedical sensors fabricated by a group of CSU electrical engineering students working with Tom Chen (Jacob Alfieri, Alden Tennison, Ming-Hao Cheng, Micheal Siegel, and Katie Wood). The sensors were fabricated using three layers of indium tin oxide (ITO), Gold/Chromium, and SU8. Each step required lithography to define the patterns, which was done using the LW405C laser writer.

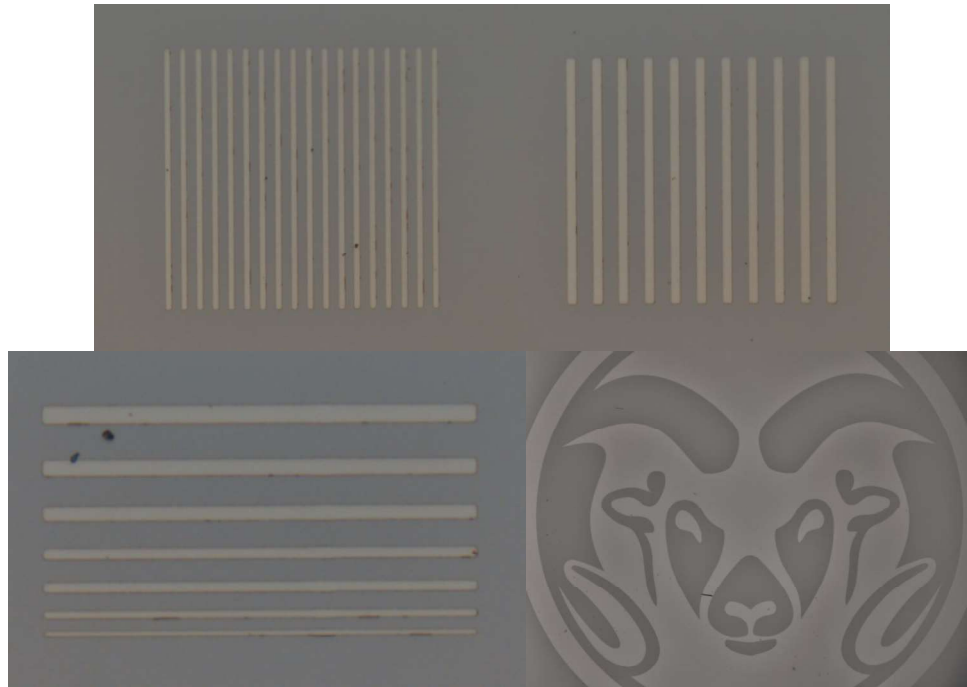


Fig. 2: Arrays of magnetic microwires were created by Kiera Thibault, a CSU physics undergraduate student working with PI Kristen Buchanan. The wires have dimensions of as small as a micron and are made of a low-damping CoFe alloy. Kiera is studying the domain formation in the magnetic micro-wires using magneto-optical Kerr effect measurements. The domain formation process is important for a planned experiment on spin wave propagation.

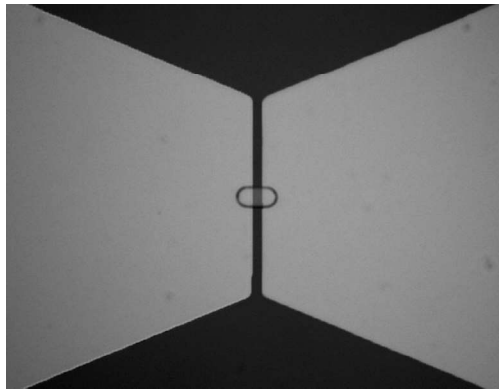


Fig. 3: A hall bar fabricated by Jinjun Ding, a CSU physics graduate student working with Co-PI Mingzhong Wu. The gap between the light-colored electrical contacts is approximately $5 \mu\text{m}$. The structure between the contacts is a Sn/CoFeB bi-layered film and this device is being used to study spin-orbit torque-induced magnetization switching in this structure. This project year a paper that made use of a similar Hall bar structure was submitted to *Scientific Advances* and accepted. The Hall bar structure in Figure 1c of the paper was used to measure the Hall resistance and the anomalous Hall resistance in the Bi₂Se₃ thin film in a Bi₂Se₃/BaFe₁₂O₁₉ bi-layered structure. It was also used to study topological surface states-induced magnetization switching in the structure.

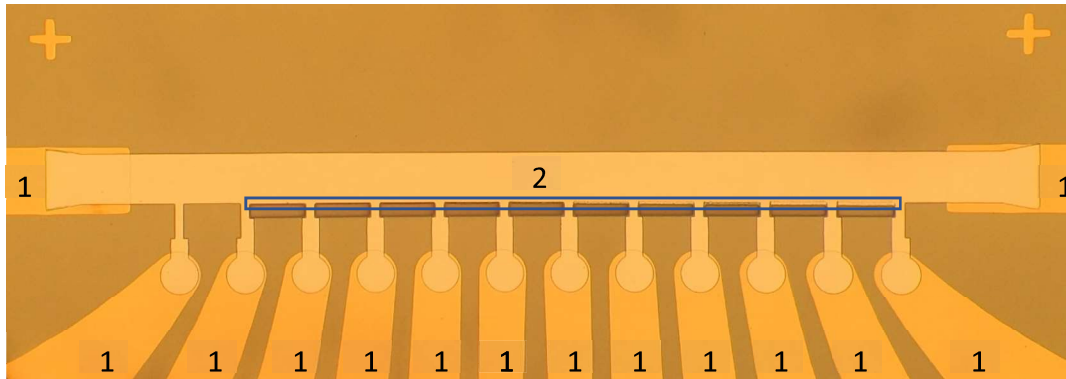


Fig. 4: Weston Maughan, a graduate student at CSU working with Co-PI Stuart Field, used the system to fabricate an 11-segment, tapered-edge superconducting sample. The laser writer was used to fabricate the gold contacts (1), a granular aluminum superconducting film (2), and to create a gradient in the thickness of the granular aluminum in the region outlined by the blue box. The thickness gradient was achieved by creating a tapered profile in the photoresist, followed by Ar^+ ion bombardment. This sample is being used to study the effects of a thickness gradient on the nucleation of superconducting vortices.

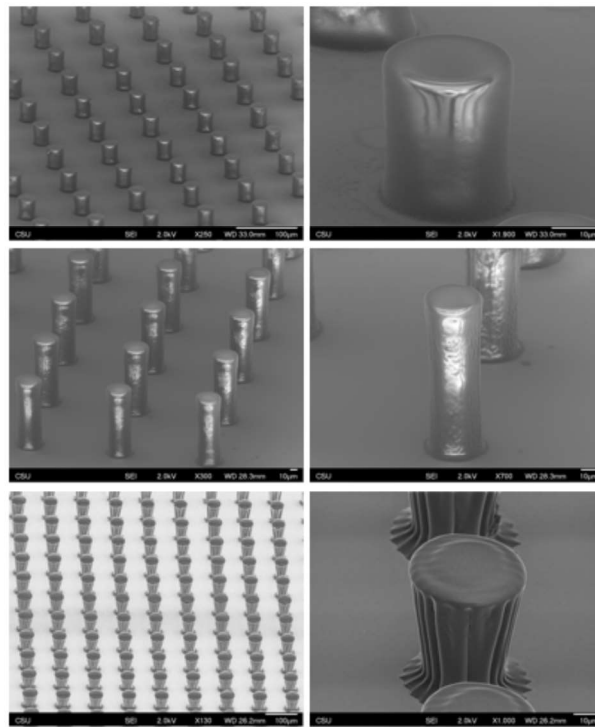


Fig. 5: Sravanthi Vallabhuneni, a graduate student from Arun Kota's group in Mechanical Engineering, has created arrays of high aspect-ratio pillars. impart the surface uniform texture for superhydrophobicity. The top and middle images show pillars with aspect ratios of 2 and 5, respectively. The bottom images show pillars with an irregular periphery that were created by using a two-step exposure, where the second exposure was done at a lower power and with a larger pattern size as compared to the first step.

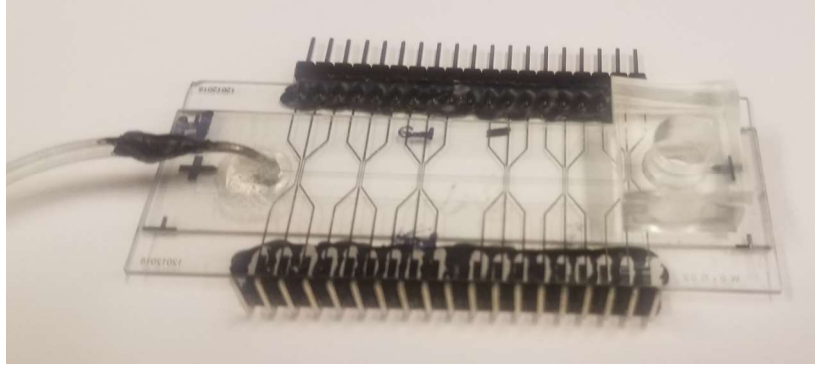


Fig. 6: Jasmine Najed, a CSU electrical engineering graduate student working with Kevin Lear's group, fabricated biosensor electrodes using a liftoff process.

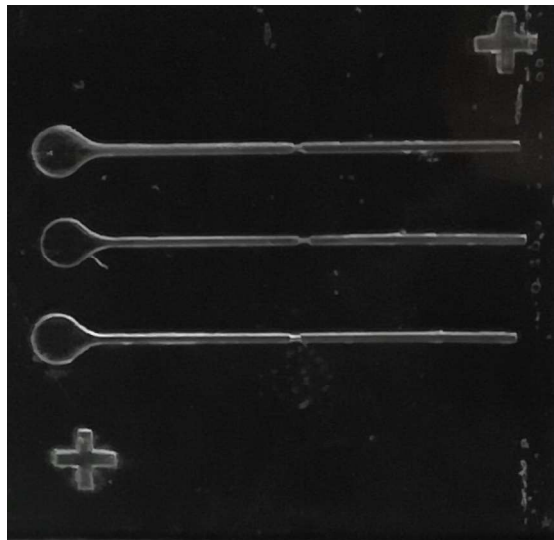


Fig. 7: Gitesh Kulkarni, a graduate student from Tom Chen's research group in the Electrical and Computer Engineering at CSU, created 80 um, 100 um, and 120 um micro-valves for microfluidics research using SU8 resist.

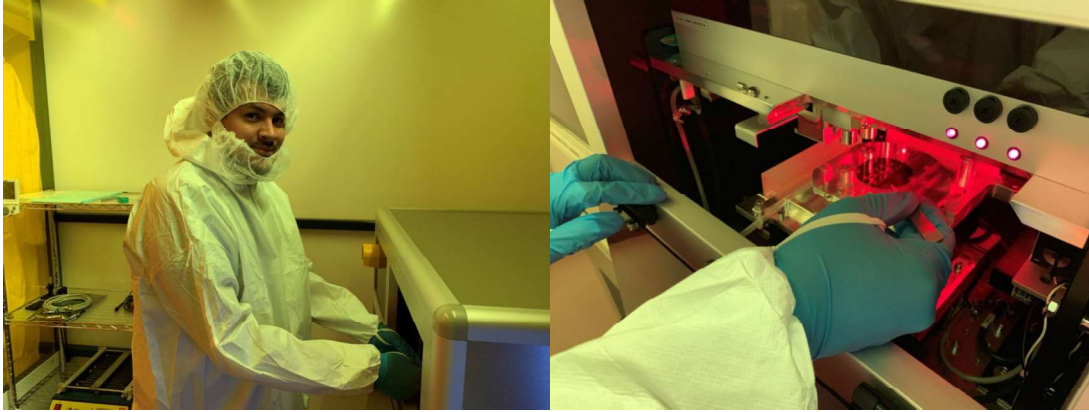


Fig. 8: Undergraduate physics student and McNair Scholar, Aron Guerrero, is shown loading a spin-coated substrated into the laser writer. Aron and his advisor, Jason Liu from Georgia Southern University, visited CSU this summer to collaborate with PI Buchanan's group and to make samples for a spin wave experiment using the laser writer. Jason is an alumni from CSU.