Annual Report for the MicroAnalytical Facility (MAF)

01 July 2017 – 30 June 2018

MicroAnalytical Facility (MAF)

Director: Paul V. Doskey

Chemical Advanced Resolutions Methods (ChARM) Laboratory

Co-Director: Lynn R. Mazzoleni
Co-Director: Michael R. Gretz

Laboratory for Environmental Analysis of Forests (LEAF)

Director: Andrew J. Burton

Molecular Biogeochemistry Laboratory (MBL)

Director: Paul V. Doskey
Abstract

The principal goal of the MicroAnalytical Facility (MAF) and associated Laboratories (i.e., ChARM, LEAF, and MBL) is to provide analyses and user access to equipment and instrumentation for elemental, ionic, molecular, and isotopic analysis for environmental, biomedical, health, and materials research. A wide variety of instrumentation is available including gas and liquid chromatographs with various detection systems and spectrometers. The volume of activity for much of the equipment and instrumentation in ChARM, LEAF, and MBL is high; however, usage varies from year to year. The LEAF and ChARM laboratories support research technical staff to assist users.
Volume I

FY 2018 Annual Report for the MAF

Purpose and Mission Statement

The MicroAnalytical Facility (MAF) is composed of the Chemical Advanced Resolutions Methods (ChARM) Laboratory, the Laboratory for Environmental Analysis of Forests (LEAF), and the Molecular Biogeochemistry Laboratory (MBL). The mission of the MAF is to provide and assist users with elemental, molecular, ionic, and isotopic analyses for environmental, biomedical, health, and materials research. The MAF supports the Michigan Tech educational mission by providing students with hands-on training in cutting-edge, trace analytical chemistry.

The ChARM Laboratory is dedicated to providing advanced research instrumentation for chromatographic separation and mass spectrometric and spectroscopic analysis of molecular and elemental species important in both basic and applied research applications. A central mission of ChARM is to provide advanced resolution measurements for environmental and biological complex mixtures, which enable research and development. The LEAF provides Michigan Tech investigators (1) expert advice on sampling and analytic techniques for chemical species in water, soil, and plant tissues, (2) supervision of students preparing samples for analysis, (3) space and equipment to perform sample grinding, extractions, filtering, and microwave digestion, and (4) analytic instrumentation for quantitative analysis of molecular and elemental composition of liquids and solids and isotopes of C and N in liquids, solids, and gases. The MBL offers Michigan Tech investigators (1) expert advice on research and development of sampling and analytic techniques for organic species in air, water, soil, and sediment matrices, (2) supervision of students for sampling, isolation, and analysis, (3) space and equipment to perform isolations from environmental matrices, and (4) analytic instrumentation for quantitative organic molecular characterization.

Core Facility Equipment and Instrumentation

ChARM - The ChARM Laboratory has a combined 3200 square feet of laboratory space in GLRC 233 of the Great Lakes Research Center and laboratories 616-618 of the Chemical Sciences Building, which were formerly designated as the Molecular Atmospheric Chemistry Laboratory (MACL). The Laboratory provides advanced research instrumentation for chromatographic separation and mass spectrometric and spectroscopic analysis of molecular, ionic, and elemental species important in both basic and applied research applications. Sample preparation and analysis by gas/liquid chromatography, mass spectrometry, ultraviolet-visible spectroscopy, and analytical microscopy is
supported. Key instrumentation and equipment available in the ChARM Laboratory includes the following, some of which are pictured below:

**Mass Spectrometry Instrumentation**

- Ultrahigh Resolution Hybrid Ion Trap Orbitrap Mass Spectrometer (Orbitrap Elite)
- Ambient Pressure Ionization Ion Trap Mass Spectrometer (LCQ Fleet)
- Gas Chromatograph/Ion Trap Mass Spectrometer
- Inductively Coupled Plasma-Mass Spectrometer

**Liquid Chromatography Instrumentation**

- Two-Dimensional, Ultra-High-Pressure Liquid Chromatograph (UltiMate 3000)
- Ultra High-Pressure Liquid Chromatograph (Accela)
- Ion Chromatograph/Dual Analysis/Cations, Anions (Dionex 2100 and 1100)
- Capillary Electrophoresis System (Beckman)

**Other Supporting Instrumentation**

- OC/EC analyzer (Sunset ECOC Analyzer)
- HD Video Microscope
- Microbalance

Thermo Scientific Two Dimensional Liquid Chromatograph/Ultra High Resolution-Orbitrap Elite Mass Spectrometer (Orbitrap Elite MS)

The Orbitrap Elite is a Hybrid Linear Ion Trap/Orbitrap mass spectrometer, which includes a dual pressure linear ion trap MS and a compact high-field Orbitrap MS with electrospray ionization, atmospheric pressure chemical ionization and atmospheric pressure photoionization sources. The instrument design enables high-quality, fast MS$^n$ characterization with ultrahigh resolution measurements (R = 240,000 at m/z 400). The 2-D UltiMate 3000 UHPLC consists of dual gradient
and high pressure gradient pumps (i.e., DPG-3000 and HPG-3000, respectively). The 2-D UHPLC supports pressures up to 620 bar at flow rates up to 10 mL min\(^{-1}\).

**Thermo Scientific High Pressure Liquid Chromatograph-LCQ Fleet Mass Spectrometer**

The LCQ Fleet Ion Trap Mass Spectrometer includes a 3-D quadrupole ion trap MS with electrospray ionization and atmospheric pressure chemical ionization sources. The instrument enables excellent full-scan sensitivity and fast MS\(^n\) characterization. The Accela LC offers flow rates up to 5 mL min\(^{-1}\) and a maximum operating pressure of 600 bar.

**Thermo Scientific Ion Chromatography System**

The ICS-2100 is a reagent-free ion chromatography system for anion analysis with conductivity detection and electrolytic eluent generation for gradient separations. The ICS-1100 system is a traditional isocratic ion chromatography system for cation analysis. The systems are run in parallel for simultaneous analyses of anions and cations.

**LEAF** - The LEAF consists of the Forest Ecology Laboratory (Horner 163), the Plant/Soil Analytical Laboratory (Horner 161), a sample preparation room (Horner
and a mass spectrometer room (Horner 163A) in Horner Hall of the U.J. Noblet Forestry Building. Together these rooms comprise a 2,200 square foot, fully functional, plant, soil, gas, and water analytical facility. In addition to analytical instruments, equipment for processing and storing samples is also available (microwave digestion, SPEX mill for grinding, walk-in cold room, and freezer). The LEAF provides analytical capabilities (1) for elemental (C, N, S, O) analysis of solids, (2) for stable isotopes of C and N in solid, liquid, and gas samples, (3) for gas chromatographic analysis of CO$_2$, CH$_4$, and phospholipid fatty acids (PLFAs), (4) for rapid flow analysis of NO$_3^-$, NH$_4^+$, and PO$_4^{3-}$ in liquids, and (5) for analysis of multiple elements (trace metals, cations) in solids and liquids. Key instrumentation and equipment available in LEAF includes the following:

Thermo-Finnigan DeltaPlus Isotope Ratio Mass Spectrometer

The Thermo-Finnigan Delta plus IRMS was purchased in 2001. The instrument has C, N, and O collectors and operates in continuous-flow mode. The peripherals are a Costech 4010 EAS with a Conflo III interface and a Thermo-Finnigan Gas Bench II. Analyses include $^{13}$C, $^{15}$N, %C, and %N of solids, $^{13}$C in atmospheric CO$_2$, and $^{18}$O in water.
The Costech 4010 ECS system was purchased in 2014 to replace an older system. The elemental analyzer is used to determine the total carbon, nitrogen, hydrogen, oxygen, and sulfur content of a sample.

The inductively coupled plasma optical emission spectrometer (ICP-OES) was purchased in 2011. The ICP-OES can be used to determine 70 different elements at concentrations below 1 mg/L, many in the mg/L range.
Shimadzu Total Organic Carbon Analyzer with Total Nitrogen Detector

The Shimadzu Total Organic Carbon (TOC) Analyzer was purchased in 2008 to replace two older instruments. The TOC analyzer is used to measure the total, organic and inorganic carbon and total nitrogen content of water samples.

Perstorp Analytical Autoanalzyer

The system was purchased in 1995. The autoanalzyer is configured to measure ammonia and nitrate/nitrite nitrogen and orthophosphate.
The gas chromatographs (GCs) were purchased in 2007 and are used to separate and quantitatively analyze compounds in gas or liquid samples. One GC has a manual injector and integrator and is currently configured for CO\textsubscript{2} analyses. The GC has a HP-Plot-U capillary column and a thermal conductivity detector. The other GC has an autosampler and ChemStation for data analysis and is currently configured for PLFA analysis. The GC is equipped with a flame ionization detector and a HP-Ultra2 capillary column. The instrument has MIDI software installed for microbial identification.

**MBL** – The MBL is located in G012 in Horner Hall of the U.J. Noblet Forestry Building. Sampling equipment is available to collect gas-, vapor-, and aerosol-phase chemical species in air. Gas-sampling valves and cryogenic preconcentration units are used to directly inject whole samples collected in glass vials, canisters, or solid sorbents to gas chromatographs for analysis of trace gases and gas-phase organic matter (OM), respectively. Vapor-phase OM collected on solid sorbents and OM in aerosol, soil, and sediment are isolated from matrices by accelerated solvent extraction. Liquid-liquid extraction is used to isolate OM from water. Solvents are reduced by accelerated solvent evaporation and nitrogen blowdown to prepare samples for analysis. A wide array of high-resolution and multidimensional gas chromatographs with a variety of detectors and an ultra high-pressure liquid chromatograph with spectrofluorometric and ultraviolet/visible detectors are available for quantitative organic molecular characterization.

Key instrumentation and equipment available in the MBL includes the following:

**Sampling Equipment**

- Automated multiport sampler for volatile organic compounds (2; custom made)
• Summa® passivated stainless steel canisters (70, 1.8 L; 50, 6 L; Scientific Instrumentation Specialists, Moscow, ID)

• Automated High-Volume Air Sampler for vapor- and aerosol-phase OM (DIGITEL DHA-80; Hegnau, Switzerland)

Isolation Equipment

• 2-Channel Supercritical Fluid Extractor (1, Spe-ed SFE-2, Applied Separations, Allentown, PA)

• Accelerated Solvent Extractor (1, Dionex ASE 350, Thermo Scientific, West Palm Beach, FL)

• Accelerated Solvent Evaporator System (Rocket™ Evaporator, Thermo Scientific, West Palm Beach, FL)

Analytic Instrumentation

• Cryogenic preconcentration, high-resolution gas chromatograph with dual flame ionization detectors for volatile organic compounds (2, custom made with HP5890s; Agilent Technologies, Wilmington, DE)

• High-resolution gas chromatograph with flame ionization and electron capture detectors (2; HP5890; Agilent Technologies, Wilmington, DE)

• High-resolution gas chromatograph with electron capture detector (1; HP5890; Agilent Technologies, Wilmington, DE)

• High-resolution gas chromatograph with thermal conductivity detector (1; HP5890; Agilent Technologies, Wilmington, DE)

• Multidimensional gas chromatograph with dual flame ionization detectors for semivolatile organic compounds (1; 6890; Agilent Technologies, Wilmington, DE)

• Multidimensional gas chromatograph with dual electron capture detectors for semivolatile organic compounds (1; 6890; Agilent Technologies, Wilmington, DE)

• Multidimensional gas chromatograph with time-of-flight mass spectrometric detector (1; Pegasus 4D; LECO Corporation, St. Joseph, MI)

• Ultra high-pressure liquid chromatograph with spectrofluorometric and ultraviolet/visible detectors (1; Dionex Ultimate 3000; Dionex, Thermo Scientific, West Palm Beach, FL)

Operational Summary

ChARM – Dr. Maryam Khaksari, the ChARM laboratory research specialist, is responsible for managing and operating the 2D-LC and high resolution Orbitrap Elite MS and associated equipment in the laboratory. The instrumentation and equipment benefit users from multiple disciplines across campus and also users
external to campus. In addition to managing the laboratory, Dr. Khaksari assists in the design and testing of analytical strategies, training users, conducting data analysis, and generating reports. The safety inspection report for FY 2018 is attached.

The Orbitrap Elite MS has been used by 15 investigators in units across campus and in one graduate level course for a total of 1264 hours following installation in November 2016. A total of 28 students have used the Orbitrap Elite for their research. Detailed information on the Orbitrap Elite use patterns by investigator and affiliated unit are summarized in Table 1. The use patterns include all

Table 1. Instrument use pattern by investigator and department for the Orbitrap Elite MS in ChARM for FY 2018.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Department</th>
<th>Activity</th>
<th>User Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynn Mazzoleni</td>
<td>Chemistry</td>
<td>MRI method development, peat fire</td>
<td>277.33</td>
</tr>
<tr>
<td>Lynn Mazzoleni (CH5241; Advanced Mass Spectrometry Laboratory)</td>
<td>Chemistry</td>
<td>Analysis of dissolved organic phosphorus</td>
<td>63.5</td>
</tr>
<tr>
<td>Paul Doskey</td>
<td>School of Forest Resources and Environmental Science</td>
<td>Analysis of dissolved organic matter in peat porewater</td>
<td>124.66</td>
</tr>
<tr>
<td>XinFeng Xie</td>
<td>School of Forest Resources and Environmental Science</td>
<td>Liquid Wood Analysis</td>
<td>25.04</td>
</tr>
<tr>
<td>Daisuke Minakata</td>
<td>Civil and Environmental Engineering</td>
<td>MRI method development</td>
<td>37.77</td>
</tr>
<tr>
<td>Martin Auer</td>
<td>Civil and Environmental Engineering</td>
<td>Analysis of personal care and pharmaceutical compounds</td>
<td>11.5</td>
</tr>
<tr>
<td>Caryn Heldt</td>
<td>Chemical Engineering</td>
<td>Osmolyte Analysis</td>
<td>105.05</td>
</tr>
<tr>
<td>Adrienne Minerick / Maryam Khaksari</td>
<td>Chemical Engineering</td>
<td>MRI method development</td>
<td>26.55</td>
</tr>
<tr>
<td>Tarun Dam</td>
<td>Chemistry</td>
<td>Unknown ID</td>
<td>1</td>
</tr>
<tr>
<td>Marina Tanasova</td>
<td>Chemistry</td>
<td>Accurate mass measurement</td>
<td>12.61</td>
</tr>
<tr>
<td>Martin Thompson</td>
<td>Chemistry</td>
<td>Peptide Analysis</td>
<td>8.5</td>
</tr>
<tr>
<td>Shiyue Fang</td>
<td>Chemical Engineering</td>
<td>Accurate mass measurement</td>
<td>20.96</td>
</tr>
<tr>
<td>Michael Mullins</td>
<td>Chemical Engineering</td>
<td>Analysis of oleic acid</td>
<td>0.5</td>
</tr>
<tr>
<td>Enterprise</td>
<td>Chemical Engineering</td>
<td>Whiskey Analysis</td>
<td>41.36</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>758.83</strong></td>
</tr>
</tbody>
</table>
charged and uncharged user times. During the first year (November 2016-June 2017), some reduced and free instrument time was offered (~20% of the time was charged) to research groups to develop a user base. In year two (July 2017-June 2017), more user time was paid by grants (~50%); however, free instrument time was provided for method development for grant proposal writing and/or exploring instrument capabilities.

The Orbitrap Elite MS use pattern including all user times (charged and uncharged) are summarized in Fig. 1. Instrument calibration and maintenance time is not charged to the users; however, on average 1.5 hours of time is required for each user appointment. The total instrument user time with respect to our capacity is plotted in Fig. 2. The use pattern for the IC system is summarized in Fig. 3.

Figure 1. Instrument use patterns for the Orbitrap Elite MS for November 2016 - June 2018.
Figure 2. Instrument use patterns for the Orbitrap Elite MS for July 2017 - June 2018.

Figure 3. Instrument use patterns for the IC System for July 2017 - June 2018.

The ICP-MS instrument in the ChARM Laboratory is currently being used for the project entitled “High Temperature Plasticity of Microalloyed Aluminum: Influence of Rapid Solidification and Wrought Processing on Precipitation Strengthening and Deformation Mechanisms” granted by Office of Naval Research (ONR). The primary investigator of the project is Dr. Paul Sanders of the Materials Science and Engineering Department. Dr. Bowen Li, Research Professor in Materials
Science and Engineering, and his PhD student, Huaguang Wang, will also be using the ICP-MS in FY 2019. Researchers from the two research groups and Dr. Khaksari worked together in FY 2018 to bring the instrument into working condition.

The GC-MS will be used for 30 hours in FY 2019 for analysis of PCBs. The project is funded through the Portage Health Foundation. The principal investigator of the study is Dr. Judith Perlinger of the Civil and Environmental Engineering Department.

The Confocal Microscope was installed in FY 2018 and a training session will be held in early FY 2019. Dr. Sangyoon Han of the Department of Biomedical Engineering is composing grant proposals for projects that will use the Confocal Microscope. The proposals, which will be submitted to NIH NIGMS, include the following:

- Nascent adhesion mechano-sensing: The study will investigate differential adhesion molecular recruitment and traction force development in cells on substrates with a wide range of stiffness.
- Shear flow mechano-transduction: The study will investigate how a monolayer of endothelial cells will respond to the laminar vs. turbulent flow in terms of traction force and cell-extracellular matrix adhesions.

The following is a list of manuscripts and conference presentations developed from the use of instrumentation and equipment in the ChARM Laboratory. The list includes 12 published, 5 submitted, and 4 in-preparation manuscripts and 18 conference presentations. Principal investigators are underlined.

### 2018 Published Manuscripts

Khaksari M, Mazzoleni LR, Ruan C, Song P, Hershey ND, Kennedy RT, Burns MA, Minerick AR, "Detection and Quantification of Vitamins in Microliter Volumes of Biological Samples by LC-MS for Clinical Screening”. AIChe J. Accepted Author Manuscript. DOI:10.1002/aic.16345


2017 Published Manuscripts


Submitted Manuscripts


Manuscripts in Preparation


Conference Presentations

Brege M, Khaksari M, Leverton T, and Mazzoleni LR, "Detection of 20,000 molecular formulas in Suwanee River fulvic acid coupling liquid chromatography to Orbitrap Elite mass spectrometry with electrospray ionization". Upper Peninsula ACS Student Research Symposium, Marquette, MI, April 2018 (Poster)
LEAF – Ms. Jennifer Eikenberry is the technical staff for LEAF. Her responsibilities include (1) controlling laboratory use and activities, (2) safety training, (3) cleaning and organizing the laboratory, (4) communicating progress of sample analyses to researchers, (5) tracking samples, (6) analyzing samples and reporting results, (7) maintaining and repairing the instruments, (8) ordering supplies, (9) billing for services, and (10) laboratory safety and chemical disposal. The safety inspection report for FY 2018 is attached.

Instrument use varies greatly by year and depends on the types of research projects and the funding available to researchers for sample processing and analysis. Usage for each instrument since user fees were established or the instrument was installed and ready for use are shown in Table 2. Details for the volume of usage over the last 6 years show the annual variation (Fig. 4). Investigators from across campus and their students have used the instrumentation over the past 6 years (Fig. 5).

Table 2. Total number of samples or elements that have been analyzed on LEAF instrumentation.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Number</th>
<th>Calendar Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCs</td>
<td>21,603a</td>
<td>May 2003 – 20 June 2018</td>
</tr>
<tr>
<td>EA</td>
<td>31,553a</td>
<td>July 2003 - 20 June 2018</td>
</tr>
<tr>
<td>DOC/TN</td>
<td>25,823a</td>
<td>May 2003 – 20 June 2018</td>
</tr>
<tr>
<td>IRMS</td>
<td>49,040a</td>
<td>August 2001 – 20 June 2018</td>
</tr>
<tr>
<td>Autoanalyzer</td>
<td>7,875b</td>
<td>January 2010 – 20 June 2018</td>
</tr>
<tr>
<td>ICP</td>
<td>44,546b</td>
<td>May 2011 – 20 June 2018</td>
</tr>
<tr>
<td>Total:</td>
<td>180,440a</td>
<td></td>
</tr>
</tbody>
</table>

aNumber of samples analyzed.
bNumber of elements analyzed.
Figure 4. Total number of samples or elements analyzed on LEAF instrumentation by fiscal year.

![Graph showing the total number of samples or elements analyzed on LEAF instrumentation by fiscal year.](image)

<table>
<thead>
<tr>
<th>Department</th>
<th>FY 12</th>
<th>FY 13</th>
<th>FY 14</th>
<th>FY 15</th>
<th>FY 16</th>
<th>FY 17</th>
<th>FY 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>523</td>
<td>150</td>
<td>196</td>
<td>0</td>
<td>0</td>
<td>1924</td>
<td>0</td>
</tr>
<tr>
<td>EA</td>
<td>1497</td>
<td>2873</td>
<td>1705</td>
<td>3374</td>
<td>2767</td>
<td>1297</td>
<td>1408</td>
</tr>
<tr>
<td>DOC/TN</td>
<td>2188</td>
<td>2756</td>
<td>3279</td>
<td>2176</td>
<td>1334</td>
<td>1257</td>
<td>1355</td>
</tr>
<tr>
<td>IRMS</td>
<td>2742</td>
<td>2116</td>
<td>1598</td>
<td>1393</td>
<td>2528</td>
<td>1333</td>
<td>1341</td>
</tr>
<tr>
<td>Autoanalyzer</td>
<td>838</td>
<td>1076</td>
<td>1540</td>
<td>548</td>
<td>355</td>
<td>604</td>
<td>334</td>
</tr>
<tr>
<td>ICP</td>
<td>6913</td>
<td>5520</td>
<td>8399</td>
<td>6608</td>
<td>4371</td>
<td>7884</td>
<td>4221</td>
</tr>
</tbody>
</table>

Figure 5. Estimated number of investigators from FY 2012 to FY 2017 by department or school who are users of LEAF instrumentation.

![Bar chart showing the estimated number of investigators from FY 2012 to FY 2017 by department or school who are users of LEAF instrumentation.](image)

<table>
<thead>
<tr>
<th>Department</th>
<th>BL</th>
<th>BME</th>
<th>CEE</th>
<th>CH</th>
<th>CHE</th>
<th>GMES</th>
<th>MEEM</th>
<th>MSE</th>
<th>SFRES</th>
<th>Outside</th>
<th>MTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EA</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>14</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>6</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IRMS</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td>12</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autoanalyzer</td>
<td>3</td>
<td></td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>13</td>
<td>12</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICP</td>
<td>6</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>9</td>
<td>1</td>
<td>3</td>
<td>13</td>
<td>12</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
The provided analyses have contributed to numerous publications. We recently asked past users of the instruments to provide a list of publications resulting from the analyses provided by LEAF. The results of the voluntary survey indicated that the data produced contributed to at least 106 peer-reviewed journal publications and 54 theses/dissertations. In just the last 5 years (2014-2018), there were 63 peer-reviewed journal publications and 31 theses/ dissertations.

**Journal Articles 2014-2018**


Jin, H., et al. (2018). "Novel high-strength, low-alloys Zn-Mg (<0.1 wt% Mg) and their arterial biodegradation." Materials Science and Engineering C 84: 67-79.


Tahtinen, B., et al. (2014). "Does ungulate foraging in forest canopy gaps produce a spatial subsidy with cascading effects on vegetation?" Forest Science 60: 819-829.


Theses and Dissertations 2014-2018


Carter, K. (2017). Effects of In-Situ Leaf-Level Canopy Warming in A Northern Hardwood Forest. School of Forest Resources and Environmental Science, Michigan Technological University. MS.


Davis, J. (2016). Vegetation Dynamics and Nitrogen Cycling Responses to Simulated Emerald Ash Borer Infestation in Fraxinus nigra-Dominated Wetlands of Upper Michigan, USA. School of Forest Resources and Environmental Science, Michigan Technological University. PhD.

del Águila-Pasquel, J. (2017). Methane Fluxes and Porewater Dissolved Organic Carbon Dynamics from Different Peatlands Types in the Pastaza-Marañon Basin of the Peruvian Amazon. School of Forest Resources and Environmental Science, Michigan Technological University. MS.

Deneau, K. (2016). The Effects of Black Locust (Robinia pseudoacacia L.) on Understory Vegetation and Soils in a Northern Hardwood Forest. School of Forest Resources and Environmental Science, Michigan Technological University. MS.


Jacobson, G. (2017). The Influence of Native Woody Species, Combretum glutinosum and Piliostigma reticulatum, on Soil Fertility in Dialacoto, Senegal. Biological Sciences, Michigan Technological University. MS.

Jarvi, M. (2015). Ecophysiological Responses of Sugar Maple Roots to Climatic Conditions. School of Forest Resources and Environmental Science, Michigan Technological University. PhD.


Kratz, C. (2014). Impacts of Climate Change on Soil Microorganisms in Northern Hardwood Forests. School of Forest Resources and Environmental Science, Michigan Technological University. PhD.

Mau, A. C. (2015). Instantaneous photosynthetic response to temperature of mature forest canopies and experimentally warmed seedlings. School of Forest Resources and Environmental Science, Michigan Technological University. MS.

Mosier, S. (2015). Interactive Effects of Climate Change and Fungal Communities on the Decomposition of Wood-Derived Carbon in Forest Soils. School of Forest Resources and Environmental Science, Michigan Technological University. MS.


Veverica, T. J. (2014). Ionic Liquid Extraction Unveils Previously Occluded Humicbound Iron in Peat Porewater. School of Forest Resources and Environmental Science, Michigan Technological University. MS.


**MBL** – Use of the UHPLC was steady in FY 2018 and supported by Drs. Doskey’s (SFRES), Minakata’s (CEE), and Datta’s (BL) projects. User fees have not been established for MBL instrumentation and equipment and instead users provide consumables for the analyses. Use of the instrumentation has been critical to the thesis projects of students in BL, CEE, and SFRES. There is no staff support for the MBL, and thus, Dr. Doskey works directly with students. The MBL is being moved, and thus, a safety inspection was not performed.
Financial Summary

The MBL has not established user fees. The ChARM Laboratory set user fees for the Orbitrap Elite MS, LCQ Fleet MS, and IC systems in FY 2016. Income and expenses for the ChARM Laboratory are summarized in Table 3. The most detailed financial information exists for LEAF, which has been in operation for several years. The income and expenses of operating LEAF are variable from year to year and based on (1) the number of samples submitted, (2) the use charge rate set by the use charge committee for a given year, (3) changes in the costs of consumables and parts, (4) large purchases and labor for major instrument repairs, and (5) increases in labor costs. A summary of the income and expenses for the last five years is presented in Table 5. There is no use charge associated with the GCs or the autoanalyzer. Users pay for consumables and labor costs.

Table 3. Income and expenses for ChARM instrumentation.

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>Orbitrap Elite MS</th>
<th>LCQ Fleet MS</th>
<th>IC System</th>
<th>OCEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY 2018</td>
<td>$11,812 / $23,914</td>
<td>$0 / $122</td>
<td>$2,834 / $5,054</td>
<td>$0/$0</td>
</tr>
<tr>
<td>FY 2017</td>
<td>$4,550 / $6,773</td>
<td>$1,560 / $6,212</td>
<td>$4,380 / $4,256</td>
<td>$0 / $617</td>
</tr>
<tr>
<td>FY 2016</td>
<td>-</td>
<td>$5,548 / $750</td>
<td>$1,850 / $0</td>
<td>$0 / $400</td>
</tr>
<tr>
<td>Total Income / Expenses</td>
<td>$16,362 / $30,687</td>
<td>$7,108 / $7,084</td>
<td>$9,064 / $9,310</td>
<td>$0 / $1,017</td>
</tr>
</tbody>
</table>

aData entries listed as Income / Expenses.

Table 4. Income and expenses for LEAF instrumentation.

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>IRMS</th>
<th>EA and DOC</th>
<th>ICP-OES</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY 2017</td>
<td>$12,586 / $12,755</td>
<td>$15,324 / $15,879</td>
<td>$23,824 / $25,919</td>
</tr>
<tr>
<td>FY 2016</td>
<td>$23,786 / $18,628</td>
<td>$15,924 / $19,211</td>
<td>$18,085 / $16,209</td>
</tr>
<tr>
<td>FY 2015</td>
<td>$12,602 / $12,250</td>
<td>$25,408 / $21,272</td>
<td>$13,687 / $14,496</td>
</tr>
<tr>
<td>FY 2014</td>
<td>$9,748 / $14,711</td>
<td>$23,674 / $27,792</td>
<td>$14855 / $16,354</td>
</tr>
<tr>
<td>FY 2013</td>
<td>$9,683 / $21,808</td>
<td>$28,881 / $29,563</td>
<td>$5,095 / $9,947</td>
</tr>
<tr>
<td>FY 2012</td>
<td>$19,845 / $17,937</td>
<td>$23,355 / $22,777</td>
<td>$8,861 / $13,047</td>
</tr>
<tr>
<td>Total Income / Expenses</td>
<td>$75,664 / $85,334</td>
<td>$132,566 / $136,494</td>
<td>$84,407 / $95,972</td>
</tr>
</tbody>
</table>

aData entries listed as Income / Expenses.

Facility Development

The MAF website (maf.mtu.edu) includes information for each of the associated laboratories. A list of available instruments and equipment for each associated laboratory and contact information for directors and staff members is posted. A detailed list of the laboratory management practices is provided for the ChARM Laboratory, which includes guidance on how to reserve instrument time, training
requirements, use rates, laboratory best practices, safety and cleanliness rules, and citation recommendations. The website was last updated in December 2017 with new hire contact information and new use charge rates. Plans are underway to further develop the website by adding a library of publications that acknowledge use of ChARM Laboratory equipment, instrumentation, and staff support.

**ChARM** – The intent was to charge user fees for most of the instrument time in FY 2018; however, some research groups continued to collect preliminary data for planned proposal submissions. The strategy helped grow the user base and provided data for publications. We will focus our efforts in FY 2019 on assisting PIs with proposal development.

Goals for the ChARM Laboratory for FY 2018:

- Continue to present and advertise ChARM capabilities to relevant departmental and interdisciplinary groups on campus.
- Provide expertise in advanced mass spectrometry methods and operation of an Orbitrap Elite, UltiMate 3000 LC System, LC/MS, GC/MS, and ICP/MS. Collaborate with university researchers and guide users in preparing and analyzing samples.
- Educate and supervise users in instrument use and data interpretation. Establish user policies, documentation, trouble-shooting protocols, and instructions on instrument operation. Help supervise and teach graduate students to use Laboratory instrumentation and equipment.

**LEAF** – A principal goal for LEAF in FY 2019 is to replace a deionized (DI) water system and for maintenance and updating of the IRMS. Funds were obtained in the FY 2019 to accomplish these goals. The DI water system, which is critical to preparing standards to calibrate the heavily used ICP-OES, is 15 years old and replacement parts are no longer available. The IRMS has experienced steady use over a period of 15 years and is central to current projects with the US Forest Service and NSF.

**Summary and Conclusions** – The MAF associated Laboratories (i.e., ChARM, LEAF, and MBL) provide and assist users with capabilities for preparation of environmental, biological, and engineered matrices for molecular, elemental, ionic, and isotopic analysis. The Facility supports Michigan Tech’s educational mission by providing users with hands-on training in cutting-edge trace chemical analyses. A wide variety of instrumentation is available including chromatographic instrumentation with various detection systems and spectrometers. There was a steady volume of activity in the MAF associated Laboratories in FY 2018; however, some instruments were utilized to a much
greater extent than others. The most heavily used instruments in ChARM, LEAF, and MBL were (1) the Orbitrap Elite MS, IC System, GC-MS, and the video microscope, (2) the IRMS, EA, ICP, and DOC, and (3) the UHPLC, respectively. The LEAF is an established Laboratory with user fees and has found success in developing a user base that is sufficient to support the operation and a research technical staff. The ChARM Laboratory and MBL were established as part of the MAF in FY 2015 and have been operating primarily by providing access to instrumentation and having users provide consumables. A research technical staff for ChARM was hired in September 2016 and user fees were established for instrumentation. A user base for the Orbitrap Elite MS was identified in FY 2018 and proposals are planned for submission in FY 2019 to support the research technical staff. Facility development in FY 2019 will include increased efforts to identify a stable user base across the MAF associated Laboratories.
Volume II

Detailed Analysis of Finance, Operation, and Development of the MAF

The LEAF was in operation long before the MAF was established in FY 2015, and thus, the focus of Volume II is on LEAF.

Facility Staff – Technical staff supporting the MAF include Dr. Maryam Khaksari (ChARM) and Ms. Jennifer Eikenberry (LEAF). Technical staff perform analyses for investigators, train students to operate equipment and instrumentation, and maintain the equipment and instrumentation in operating condition. Support for their positions is derived from user fees for LEAF and ChARM equipment and instrumentation.

Detailed Operational Analysis – Usage of the major instruments in LEAF varies from year to year (Fig. 4). Projects for which the GCs were purchased have concluded, and thus, usage is low. However, there is a project that plans to use a GC for PLFA analysis in FY 2019. The autoanalyzer is used every year; however, the frequency of use is low due to the large amount of time and labor that is required to prepare the instrument and reagents for analysis. The total number of samples analyzed on the ICP-OES was lower in FY 2018 than FY 2017; however, daily usage of the instrument was not lower. The number of sample submissions for the ICP-OES in FY 2018 was about the same. In FY 2018, there were 113 requests for analyses and an average of 37 samples per request. In FY 2017, there were 93 requests for analyses and an average of 85 samples per request, which resulted in a higher overall number of samples analyzed in FY 2017. The difference in number of samples analyzed is due to more use of the ICP-OES for chemistry and engineering research and less use for biology and ecology research, which typically requires more analyses per request.
Safety Analysis and Corrective Action –

ChARM – The inspection for FY 2018 was conducted by Environmental Health and Safety on February 12, 2018. A summary of items to be corrected and the actions taken are presented in Table 1.

Table 1. Items to be corrected and actions taken in GLRC 223.

<table>
<thead>
<tr>
<th>Items to be corrected</th>
<th>Actions taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum of 36” clearance for electrical panels.</td>
<td>Electrical panel controlled through panel on UPS system. There is now appropriate clearance for electrical panels. Completed 02/12/2018.</td>
</tr>
<tr>
<td>Fume hood in Rm 219 not balanced with room air.</td>
<td>Hood sash needs to be opened more slowly to prevent momentary unbalancing. Inspection completed by Facilities Management (03/02/2018).</td>
</tr>
</tbody>
</table>

LEAF – The inspection for FY 2018 was conducted by Environmental Health and Safety on February 2, 2018. A summary of items to be corrected in Laboratories 161, 163, and 191 and the actions taken are presented in Table 2.

Table 2. Items to be corrected and actions taken in the LEAF Laboratories.

<table>
<thead>
<tr>
<th>Items to be corrected</th>
<th>Actions taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low molecular weight polyethylene glycol (PEG 300 or PEG 400) should be available for first aid.</td>
<td>PEG is available for phenol exposure. Completed 04/10/2018.</td>
</tr>
<tr>
<td>Need to check hood operation in relation to make up air going into room. Room 163 should be negative in relation to the adjacent lab.</td>
<td>Facilities made adjustments to the make-up air. Work Order 99010 completed 03/08/2018.</td>
</tr>
<tr>
<td>Make sign “official” so that everyone knows electrical panel cannot blocked.</td>
<td>A sign was re-printed. Completed 02/13/2018.</td>
</tr>
<tr>
<td>Replace the guard on the grinder mill.</td>
<td>Guard replaced. Completed 02/13/2018.</td>
</tr>
<tr>
<td>Fix the back of the lab chairs.</td>
<td>The backs of chairs were repaired or removed. Completed 02/07/2018.</td>
</tr>
<tr>
<td>Make the label clearer on the aqueous stable isotope reference materials for water.</td>
<td>Re-labeled to make it clear that the reference materials are water and non-hazardous. Completed 02/07/2018.</td>
</tr>
</tbody>
</table>

MBL – The MBL is being moved from the Dow building, and thus, the Laboratory was not inspected.

Detailed Income and Expense Analysis – Income for the LEAF facility comes solely from user fees (Tables 3-5). Contracts from government researchers and
other university investigators are charged the standard user rate for sample analysis plus the required overhead.

Table 3. Combined expenses and income for the isotope ratio mass spectrometer (IRMS) for FY 2012 – FY 2018.

<table>
<thead>
<tr>
<th></th>
<th>FY 2012</th>
<th>FY 2013</th>
<th>FY 2014</th>
<th>FY 2015</th>
<th>FY 2016</th>
<th>FY 2017</th>
<th>FY 2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income</td>
<td>$19,845</td>
<td>$9,683</td>
<td>$9,748</td>
<td>$12,602</td>
<td>$23,786</td>
<td>$12,586</td>
<td>$14,906</td>
</tr>
<tr>
<td>Clerical/Technical</td>
<td>$9,385</td>
<td>$10,081</td>
<td>$6,436</td>
<td>$4,585</td>
<td>$8,565</td>
<td>$4,729</td>
<td>$7,847</td>
</tr>
<tr>
<td>Fringe Benefits</td>
<td>$3,402</td>
<td>$3,831</td>
<td>$2,510</td>
<td>$1,674</td>
<td>$3,212</td>
<td>$1,773</td>
<td>$3,061</td>
</tr>
<tr>
<td>Services</td>
<td>$518</td>
<td>$679</td>
<td>$570</td>
<td>$258</td>
<td>$0.10</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Supplies-gases</td>
<td>$4,475</td>
<td>$2,509</td>
<td>$2,856</td>
<td>$3,272</td>
<td>$3,437</td>
<td>$2,338</td>
<td></td>
</tr>
<tr>
<td>Supplies-parts,</td>
<td>$1,529</td>
<td>$1,855</td>
<td>$1,529</td>
<td>$2,572</td>
<td>$1,776</td>
<td>$1,961</td>
<td></td>
</tr>
<tr>
<td>chemicals, consumables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas cylinder rental</td>
<td>$1,212</td>
<td>$832</td>
<td>$1,349</td>
<td>$1,005</td>
<td>$1,040</td>
<td>$1,013</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Combined expenses and income for the inductively coupled plasma optical emission spectrometer (ICP-OES) for FY 2012 – FY 2018.

<table>
<thead>
<tr>
<th></th>
<th>FY 2012</th>
<th>FY 2013</th>
<th>FY 2014</th>
<th>FY 2015</th>
<th>FY 2016</th>
<th>FY 2017</th>
<th>FY 2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income</td>
<td>$8,861</td>
<td>$5,095</td>
<td>$14,855</td>
<td>$13,688</td>
<td>$10,685</td>
<td>$23,824</td>
<td>$20,311</td>
</tr>
<tr>
<td>Clerical/Technical</td>
<td>$6,320</td>
<td>$3,571</td>
<td>$6,335</td>
<td>$6,084</td>
<td>$7,576</td>
<td>$11,854</td>
<td>$13,185</td>
</tr>
<tr>
<td>Fringe Benefits</td>
<td>$2,291</td>
<td>$1,357</td>
<td>$2,471</td>
<td>$2,221</td>
<td>$2,841</td>
<td>$4,445</td>
<td>$5,142</td>
</tr>
<tr>
<td>Supplies-gases</td>
<td>$2,120</td>
<td>$2,873</td>
<td>$4,515</td>
<td>$3,213</td>
<td>$3,439</td>
<td>$5,844</td>
<td>$3,810</td>
</tr>
<tr>
<td>Supplies-parts,</td>
<td>$1,483</td>
<td>$1,131</td>
<td>$2,048</td>
<td>$1,431</td>
<td>$1,271</td>
<td>$2,025</td>
<td>$2,287</td>
</tr>
<tr>
<td>chemicals, consumables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas cylinder rental</td>
<td>$834</td>
<td>$875</td>
<td>$986</td>
<td>$1,548</td>
<td>$1,079</td>
<td>$1,750</td>
<td>$1,132</td>
</tr>
</tbody>
</table>
Table 5. Combined expenses for the total organic carbon analyzer (DOC) and elemental analyzer (EA) for FY 2012 – FY 2017.

<table>
<thead>
<tr>
<th></th>
<th>FY 2012</th>
<th>FY 2013</th>
<th>FY 2014</th>
<th>FY 2015</th>
<th>FY 2016</th>
<th>FY 2017</th>
<th>FY 2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Income</td>
<td>$23,355</td>
<td>$28,881</td>
<td>$25,408</td>
<td>$25,408</td>
<td>$15,924</td>
<td>$15,324</td>
<td>$16,464</td>
</tr>
<tr>
<td>Clerical/Technical</td>
<td>$11,800</td>
<td>$17,063</td>
<td>$15,809</td>
<td>$10,824</td>
<td>$9,817</td>
<td>$7,172</td>
<td>$9,679</td>
</tr>
<tr>
<td>Fringe Benefits</td>
<td>$3,947</td>
<td>$5,320</td>
<td>$6,122</td>
<td>$3,951</td>
<td>$3,682</td>
<td>$2,690</td>
<td>$3,775</td>
</tr>
<tr>
<td>Supplies-gases</td>
<td>$2,533</td>
<td>$3,925</td>
<td>$3,400</td>
<td>$3,586</td>
<td>$3,923</td>
<td>$2,439</td>
<td></td>
</tr>
<tr>
<td>Supplies-parts,</td>
<td>$3,644</td>
<td>$1,507</td>
<td>$2,275</td>
<td>$1,414</td>
<td>$1,410</td>
<td>$1,718</td>
<td></td>
</tr>
<tr>
<td>chemicals, consumables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas cylinder rental</td>
<td>$870</td>
<td>$429</td>
<td>$822</td>
<td>$712</td>
<td>$682</td>
<td>$552</td>
<td></td>
</tr>
</tbody>
</table>

Internal funding for MAF for FY 2019 included an award of $87,806. The funding will be distributed as follows: $10,200 for repair of the LC/MS in the ChARM Laboratory, $49,892 for ChARM Laboratory user fees, $16,671, for maintenance required on the IRMS in LEAF, $5,935 for replacement of the DI water system in LEAF, and $5,108 to erase the FY 2018 deficit.

Developmental Plans—Developing a stable user base that is sufficient for full funding of technical staff for the MAF associated laboratories is the principal goal for future development of the shared facility. A fully developed MAF will require technical staff to manage activities of LEAF and ChARM. The LEAF has been successful at operating via user fees and partially offsetting the salary of a technical staff. The technical staff for the ChARM Laboratory will be partially supported in FY 2019 via the FY 2019 core facility award. Sufficient user fees will have to be charged to fund the balance of the technical staff’s salary.

A principal goal for LEAF in FY 2019 is to have a pool of funds immediately available when needed for non-routine repair of instruments. The funds would be used for manufacturer’s service technicians, repair parts, and tools for major problems that are not a part of routine maintenance or considered consumable parts replacements. Examples may be replacements of electrical circuit boards, computers, or a failed vacuum pump. Instruments can be out of service for months while trying to obtain funding for troubleshooting and repairs, which results in a delay in getting data to researchers, or the researchers sending their samples to another institution. Also, if repairs are not made when they are needed, it could result in more costly repairs in the future. Instrument use charges can be used for this purpose; however it is not permitted to generate a surplus of funds from instrument use charges, so if repairs and service are
performed, it creates a large deficit in the use accounts. Increasing use fees, using departmental funds, or the overhead return on the use charge index must be used to erase the deficit. Changing the use fees from year to year to make up for these occasional large expenditures is difficult for researchers who have budgeted a specific amount of funds for sample analyses. Departmental funds are not appropriate to use to support shared facilities that are used by the entire university community. Overhead return accounts generated from use charges typically do not contain sufficient funds for major repairs.

**Risks and Challenges –**

The greatest challenge for the MAF is creating a sufficient cash flow to keep instruments and equipment running and to cover the salary of technical staff. Including maintenance and instrument replacement in user fees drives up the per sample costs to users making it difficult to remain competitive. Meeting the challenge with the only source of support being soft money is particularly difficult in the early stages of the Facility development. Offsetting some of the salary of technical staff through unit funds would help in this regard.

An additional challenge, which was realized in FY 2017, was the loss of space for the MBL due to University policy that allows units to buy and sell space. Space is designated as “University space”, and thus, the ability of a unit to buy and sell space, and in particular shared facility space, runs counter to the designation of space as “University space”. Unlike laboratory space occupied by Tech faculty, shared facilities are a resource, which are available to investigators and students across campus, including those of the unit in which the shared facilities are located. Thus, allowing a unit to sell space occupied by a shared facility runs counter to the mission of the shared facilities. In addition, moving a shared facility from a laboratory with infrastructure uniquely developed for its purpose to another laboratory where the infrastructure must be duplicated is a waste of Tech resources and the time of the director of the associated laboratory of the shared facility.

**Summary Comments** – The LEAF was in operation long before the MAF was established in FY 2015, and thus, the focus of Volume II is on LEAF. The MAF currently has two research technical staff responsible for activities in LEAF and ChARM. Use of instrumentation in LEAF varies from year to year with no overall trends in use. All items identified in the annual safety analyses of the MAF associated Laboratories that required attention were corrected. User fees support operation of LEAF. An FY 2019 internal award ([$87,806]) for MAF will be used to support a research technical staff for ChARM and maintenance and replacement of equipment in LEAF. The principal development plan for MAF continues to be identifying a stable user base to support technical staff to handle the volume of activity in the MAF associated Laboratories.