Project Title: Reducing Chemical Waste in the Chemistry Department
Budget Requested: $ 40,318
Project Members:

Cyril Vallet: Applicant/Project Manager (project applicant)
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Professor Jean-Philip Lumb: Project and Lab Supervisor (project applicant)
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Christian Bouchard: Project Supervisor, Manager (project applicant)
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Professor Tomislav Friscic: Lab Supervisor
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Professor Audrey Moores: Project Consultant
Ted Hunter – Lumb Lab Assistant
Kale Laviolette – Friscic Lab Assistant
Environment/Economics Intern (part-time) – *Interviews in progress*

I. Project Overview

Project summary:

This project takes an interdisciplinary approach to minimize the total output of chemical waste produced in the McGill Chemistry Department. Some information is available on the quantity and composition of current chemical waste streams. Hazardous Waste Management (HWM) and chemistry faculty members (Professor Christopher Barrett) have identified current practices associated with high costs in graduate and undergraduate labs. This work revealed that the use of organic solvents created the highest volume of waste. The project will build on previous projects such as the SPF funded 'Hazardous Waste Minimization (SP0025)', 'Hazardous Chemicals Disposal Campaign (SP0032)', and 'Chemical Curriculum Development (SP0068)'

This proposal incorporates top-down and bottom-up approaches to identification implementation of energy and cost saving solutions. Students will work collaboratively with professors, their research laboratories and staff, receiving frequent supervision and guidance via a unique, multi-disciplinary learning environment. Arguments for safety, monetary savings, and education will be used to ensure the long-term implementation of our recommendations.

Specifically, two undergraduate lab assistants will use part of their time to monitor the waste output of two laboratories by segregating waste streams and extrapolating their data for the long term. A model for waste segregation will be developed and applied. The model will be designed for future application to other labs. An economy student will carry out a cost benefit analysis to determine if a solvent recycling program is feasible and on what scale. Additionally, we will study the waste outputs of undergraduate labs. We will determine if those labs would benefit from a solvent recycling program and modified lab procedures. Minor adjustments suggested by HWM will also be tested. They include solvent pumps to prevent excess solvent use and in-lab acid-base neutralization.

Project eligibility:

Due to the interdisciplinary nature of this project, new lines of communication will be developed. Professors, staff, and students will pool their resources and expertise to produce alternatives to conventional chemical waste disposal habits and treatments. Additionally we will propose changes to HWM's hazardous waste disposal training to include procedures that compliment a solvent recycling program and appropriate waste segregation protocols. The final report will include a comprehensive assessment of a solvent recycling program, a green lab procedure for organic chemistry, and a model for hazardous waste minimization that can be applied to other labs. In this way, the culture around hazardous waste will be affected through educational and administrative means.

It is important to convey that such a project is only a small part of the overall hazardous waste minimization effort at McGill. The project manager will ensure that efforts continue through student research, research lab participation, and with administrative support. A committee of stakeholders will be put together for regular meetings so these efforts are continued and well informed in the future.

Timeframe/Milestones:

Since the project involves monitoring lab waste in the Lumb and Friscic Lab, we will have a good idea of the quantity of waste coming from those labs by July 1st. The goal of the project is not only to reduce the waste from these labs within summer but to determine which improvements will have an impact and how to implement them throughout the department. We will document short-term reductions and projected reductions in waste throughout the summer. The waste monitoring will also be set up for longer term use. Once a solvent recycling program is in place, the true reductions in waste can be reported from all participating labs. The new committee will ensure that these assessments happen.

Start: May 6st 2013

June 3rd, 2013

- Previous research and reports have been compiled from both scientific literature and past projects. The information includes
    - preliminary summary quantity/composition of chemical waste
    - reports on chemical waste projects in other universities
    - background research on equipment and procedures
    - list of chemicals and equipment needed for waste segregation
- Waste audits pertaining to the solvent recycling program and solid waste assessments in the Lumb and Friscic labs are underway

July 1st

- Potential structures for a solvent recycling program has been created
- Economic and environmental assessments of the chemistry department's hazardous waste has been carried out
- Waste segregation and treatment methods for research labs have been identified and are being tested in two labs

July 29th
- A cost benefit analysis of waste segregation has been carried out
- A plan has been proposed for several undergraduate labs to implement waste treatment in their procedures
- A Chemistry Hazardous Waste Committee is formed and agrees to pursue recommendations

August 30th, 2013
- A cost benefit analysis of the proposed solvent recycling program has been carried out
- A pamphlet for labs summarizing our efforts and recommendations has been printed (time permitting)
- A report on short-term and long-term implementation strategies has been created and the financial and environmental benefits have been determined for the
    - solvent recycling program
    - undergraduate lab modifications, curriculum modifications
    - waste segregation and treatment methods for research labs

Stakeholders:
- Hazardous Waste Management (Christian Bouchard)
    - background knowledge, previous reports [confirmed]
- Environment Health and Safety (Wayne Wood)
    - background knowledge
- Maass Chemistry Building (Director: Normand Trempe)
- McGill Chemistry Department
    - Department Chair: Bruce Lennox
    - Director of Undergraduate Studies: Sam Sewall
        - dissemination of information [confirmed]
    - Undergraduate Lab Managers (Mitchell Miller, Jean-Marc Gautier)
        - cooperation, implementation of alternatives
    - Professor Christopher Barrett
        - project oversight, implementation of recommendations [confirmed]
- Facilities Operations and Development (Jerome Conraud)
    - informational resources, advice on project management [confirmed]

In the long run, thousands of chemistry students will learn new techniques in green chemistry and improved ways of handling hazardous waste. Also, research labs will be shown ways to save money and chemicals through waste minimization and recycling.

II. Project Implementation

Tasks and Responsibilities:

NOTE: Cyril's weeks are near full-time, Kale and Ted's weeks are part-time and the Econ/Envr intern's weeks are part-time. Biweekly meetings will be held to ensure that

team members are on task and communicating. PowerPoint style summaries of current work are expected from students on a regular basis.

Type of Activity – Task	**Estimated Time**	**Group Member**
Project management	ongoing	Cyril
Outreach and presentations	ongoing	Cyril
Help design solvent and solid waste segregation/treatment methods with Kale and Ted	3 weeks	Cyril
Research previous efforts in other universities	2 week	Cyril
Design solvent recycling program	4 weeks	Cyril
Create chemical waste committee	2 week	Cyril
Ensure continuation of efforts through student research and stakeholder collaborations	3 weeks	Cyril
Write final report	2 weeks	Cyril
Design green lab for organic chemistry	6 weeks	Kale
Study solid waste output from Friscic Lab	6 weeks	Kale
Study treatment and recycling of heavy metals, silica gel, ethidium bromide and others	3 weeks	Kale
Assess feasibility of using carbon filters	1 week	Kale
Develop waste treatment procedures for undergraduate organic chemistry labs	6 weeks	Ted
Study solvent waste output from Lumb Lab	6 weeks	Ted
Study treatment and recycling of acids and bases, chromatographic solvents	3 weeks	Ted
Assess feasibility of using solvent pumps to minimize over-pouring	1 week	Ted
Carry out economic and environmental assessment on hazardous waste in the department	8 weeks	Econ./Envr. Intern
Analyze costs and benefits of solvent recycling and hazardous waste treatment options	8 weeks	Econ./Envr. Intern

III. Financials

Critical Date: May 6th, 2013

Expenses:

Expense Description	**Estimated Cost**
Project Manager Stipend – 12$/h, 32h/week, 16 weeks	$ 6144
Student Lab Assistant Stipends – 12$/h, 60h/week, 16 weeks equivalent to 1.5 full-time students	$ 11,520
Economy/Environment student intern stipend – 12$/h, 20h/week, 16 weeks	$ 2304
Chemicals, lab consumables, instrument operation	$ 20,000
Administrative costs (printing, phone calls, office supplies)	$ 350

Revenues:

Revenue Source	**Amount Requested**	**Confirmed?**
Sustainability Projects Fund	$40,318	No

IV. Additional information:

Chemistry Faculty Letter of Support
Project Applicant/Manager Resume
Project Applicant/Manager Previous Research
Chemical Curriculum Development SP0068
Hazardous Waste Minimization SP0025
Hazardous Chemicals Disposal Campaign SP0032

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Monday, March 11, 2013

Re: Application for SPF-support, Summer 2013

Dear Office of Sustainability,

The following application, co-authored with Cyril Vallet and Christian Bouchard, requests funding for the salary of students and consumables for the duration of our project, which seeks to minimize the quantity of waste produced by the Chemistry Department at McGill University. Currently, the Chemistry Department produces 25% of the hazardous waste generated on the downtown campus (Bohman/Bouchard SP0025). Therefore, this project will dramatically improve the overall sustainability of the University, by improving waste management in one of the largest emitters on campus.

Our proposed team is representative of the McGill Community, and is composed of faculty, staff and students. We propose a multi-dimensional approach to waste minimization, which capitalizes on previous efforts within the department to assess waste generation. We are ideally positioned to begin pilot projects at both the graduate and undergraduate levels in the areas of waste segregation and recycling. Both of these aims will provide immediate reductions to the cost and volume of waste treatment. We are also proposing new experiments for the introductory organic chemistry laboratories (~2000 students/year), which will replace current modules with solvent-free alternatives. Finally, we will investigate the current environmental footprint of the department, with the goal of setting a long-term agenda, striving for a State-of-the-Art learning environment with zero-emissions.

The Department of Chemistry has several faculty members who will work with me to mentor our summer staff. These members will include Professors Audrey Moores, Tomislav Friscic and Christopher Barrett. This letter confirms their support. Bi-weekly meetings will be held to monitor progress, and to chart novel directions. In addition, collaboration with Christian Bouchard and Wayne Wood in the Office of Hazardous Waste Management will ensure the feasibility and rapid implementation of our proposed solutions. Taken together, the project provides an ideal learning environment for students to see a complete life-cycle analysis of the chemical process, and to take part in pedagogical development.

We hope that you will consider this project favorably, and look forward to hearing your response.

Jean-Philip G. Lumb, Ph.D.
Assistant Professor of Chemistry

Green Chemistry Opportunities in Chemistry Research Labs

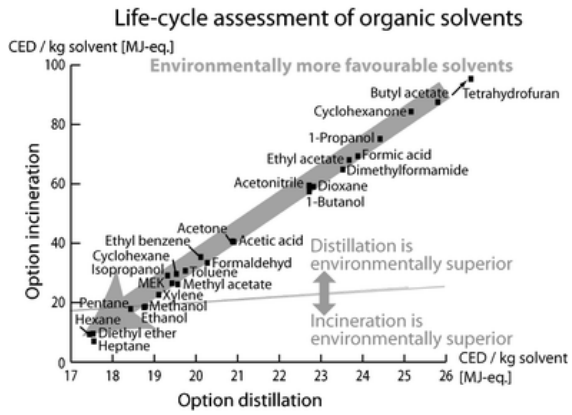
Cyril Vallet

Background. Green Chemistry is rapidly gaining interest in academic and industrial research labs. Funding agencies are becoming more concerned with exploiting academic research to address 'quality-of-life issues'.[5] As a result, Green Chemistry plays an important role in the voluntary 'responsible care' program for safety and sustainability in industry.[6] The 'sustainable development' concept has been adopted by Green Chemistry with an interdisciplinary approach. Still, sustainable progress needs to be hastened by coupling development of processes or materials with managerial, environmental, and political mechanisms.[7] US academic research and development (R & D) spending for chemistry and chemical engineering came to 2.3 billion USD in 2009.[8] In US industries, chemistry R & D spending totaled to 7.1 billion USD in 2009.[9] Spending continues to increase annually. [8-9] While chemistry provides an enormous amount of cleaner alternative syntheses for industry, chemistry research labs (incorporating 'sustainable development' or not) can generate lots of waste and consume large amounts of energy.

While chemistry research expands both in industry and academia, the amount of waste will also grow if it is not regulated. Any chemicals that cannot go down the drain are collected through hazardous waste management. Typically, non-chlorinated waste gets burned for minimal energy recovery and chlorinated waste is incinerated at high temperature to reduce formation of dioxins. These processes can take up a significant amount of energy while also releasing pollutants. The alternatives such as distillation or filtration can also come at a high energy cost. There are many chemical techniques that help reduce the waste generated in the first place. Some decisions can be made qualitatively by the researcher, based on the ACS 12 Principles of Green Chemistry and green chemistry metrics. Lifetime cycle analysis can be preformed for more quantitative, result-based decisions. This report focuses on opportunities for researchers to implement green chemistry, while not necessarily doing research for green chemistry.

Handling Solvent Waste. The most available green chemistry opportunity in chemistry research is reducing the impact of solvent waste. In the spirit of sustainablility, three methods can be implemented: reduce, reuse, recycle. These include simple procedures like re-using oil from oil baths, using vacuum pumps instead aspirators[10] not letting solvents expire before use, and taking only what you need from stock containers. However, there are additional chemistry approaches such as recycling solvents by distillation or filtration, choosing 'greener' solvents, or avoiding solvent use whatsoever.

Small scale distillations are often not energy or time-efficient[10]. In this case, research is available to help you determine which is the 'greener' solvent. Capello et al. provide a "framework for the environmental assessment of solvents".[2] Environmental health and safety (EHS) and life-cycle assessment (LCA) methods are carried out and combined. The EHS method relies mainly chemical properties such as toxicity, persistency, and other environmental and safety aspects. The LCA however looks at the whole life cycle of a solvent including production energy costs and waste treatment costs such as distillation or incineration.



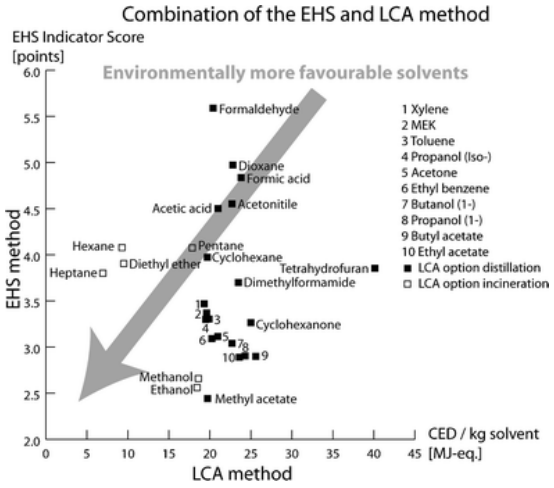


Figure 1: EHS and LCA data for solvents[2]

Garrigues et al.[4] suggest that although remediation techniques are often researched for industrial application they can also apply on a laboratory scale. Analytical techniques such as liquid chromatography consume high amounts of organic solvent as the mobile phase. One solution is a closed-loop eluent-recycling system where the mobile phase is immediately recirculated after the analyte is adsorbed by activated carbon. Another solution is to distill the solvent waste. B/R Instrument Corporation has designed an automated fractional distillation system for the manual recovery of solvents. There is the obvious drawback of distilling azeotropes such as ethanol and acetonitrile that will produce solvents of lower purity than the original stock.

Green Chemistry Metrics

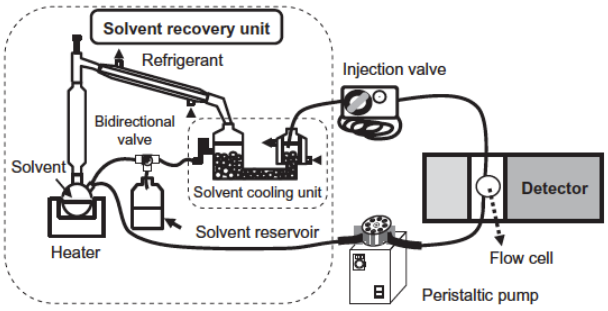


Figure 2: Solvent distillation system[4]

Some important calculations can be made from reactions schemes and data that allow the researcher to quantify the fundamental energy and environmental costs of a reaction. Traditionally, calculations are done to determine the yield of a reaction (RY) and selectivity. These provide a gauge of how much product is obtained compared to a theoretical maximum. However, if you decide to perform a double displacement reaction, you may end up with 100% yield while still having large amounts of by-products. The following green chemistry metrics allow the researcher to design of reactions that better conserve resources.

(mass of desired product = mdp)

Atom Economy (AE)= (*theoretical mdp)/(mass of all reactants)*

E-Factor (AE) = *(actual mass of waste*)/(actual mdp)*

Reaction Mass Efficiency (RME)= *(actual mdp)/(mass of all reactants) X 100%*

Mass Intensity = *(total mass for reaction*)/(actual mass of desired product)*

**may or may not include solvent*

***includes solvent*

These parameters can be arranged in a pentagonal form to give a visual representation for choosing the reaction method. Below is an example for Grignard reaction for diphenyl methanol under various scenarios.[3] It also includes a material recovery parameter (MRP) and stoichiometric factor (SF) that take into account excess reagents and post-reaction materials such as washings and extraction solvents.

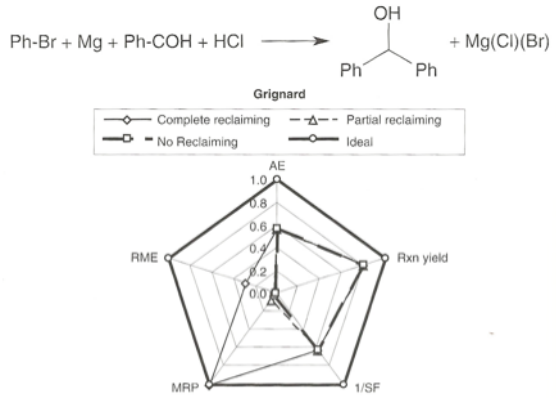


Figure 3: Radial pentagon representing green metrics for grignard reaction above[3]

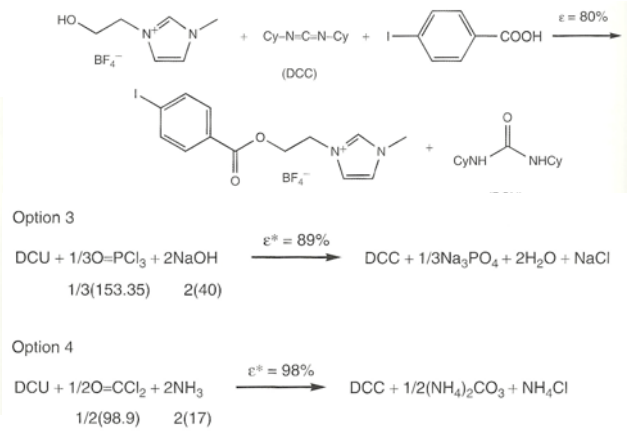


Figure 4: Recycling options for DCU to DCC from the reaction above

Another optimization strategy is adding a recovery step such as converting a by-product back into a starting material. Below is a reaction that produces DCU that can be converted back to DCC by several methods shown in in Figure 4. The authors of Green Chemistry Metrics[3] combine reaction yield with mass intensity to determine (RY– MI) that 'Option 4' has the largest value and is best suited for use to recover DCC. There are many more green chemistry metrics that can be used to help researcher chose which reaction is less environmentally harmful.

Handling Hazardous Contaminants. Before beginning to pile up hazardous waste in the lab, it is important to consider whether the waste needs to be dealt with by hazardous waste management (with incurring costs, energy of transportation, and adding volume to hazardous waste). UBC has compiled a list of chemicals safe to dispose of down the drain (with lots of water) or in the garbage. It includes ethylene glycol, oleic acid, squalane, ascorbic acid, sodium phosphate/sulfate and many more.[11]

There will inevitably be hazardous waste leftover that cannot be reused. Often it is transported and stored before eventually being incinerated. Toxic heavy metal and CO emissions coupled with green house gas emissions of transportation is not favorable.[4] Garrigues et al. suggest using a GC column to thermally compose waste after the analysis is complete. Hydroxy radicals can be used to oxidize organic compounds using the Fenton reagent with removal efficiencies well above 99%.[4, 12]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\cdot$$

This procedure can be done to aromatic carcinogenic amines in water at room temperature. The procedure results in the benign water, oxygen, ferric hydroxide and the precipitates from ring cleavage or mineralization products. The precipitates can be further oxidized in much smaller volumes by the Fenton reagent.

Photocatalytic oxidation can also be used to convert toxic anions such as nitrite, sulfite, and cyanide to the less toxic nitrate, sulfate, isocyanide. TiO_2 can be fixed onto polymer

membranes or borosilicate glass and reused to catalyze the oxidation.[4] Frank et al.[13] have reported the following conversion >99% using TiO_2 and sunlight.

Handling Persistent Chemicals in Waste. Some waste, such as heavy metals, cannot be degraded. The coprecipitation method can be used to remove heavy metals such as mercury and silver. Coprecipitation occurs when a solute either adsorbs to a precipitate, gets trapped by the precipitates crystal structure or is included in the structure. Cava-Montesinos et all conduct coprecipitation of Hg(II) with $Fe(OH)_3$ after an atomic fluorescence experiment to reduce their waste from 1 liter of mercury-contaminated solvent to 1 gram of solid waste.[14]

Green Chemistry Research Techniques

Many new techniques are being developed by Green Chemistry labs for larger scale use. Any chemistry lab can incorporate these ventures in their own research. Solvent-free syntheses are one of the most direct ways to reduce lab waste. In parallel, microwave radiation provides an energy efficient way to provide energy for a reaction. Tanaka summarizes many examples of solvent free synthesis under microwave irradiation in the book, Solvent-free Organic Synthesis.[1] Above is an example of a cross-Cannizzaro reaction for the reduction of an aldehyde to an alcohol. One drawback of this reaction, however, is poor atom economy. The formaldehyde is oxidized to sodium formate.

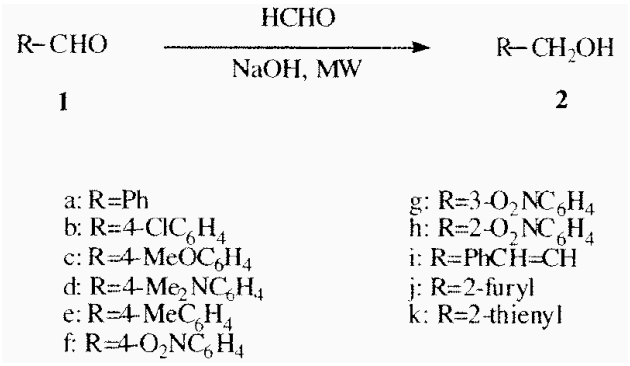


Figure 5: Solvent-free, microwave induced reduction[1]

Catalysis is a very effective way to improve atom economy. Catalyst recovery lies within the 1st and 9th principle of green chemistry: preventing waste while utilizing catalysis. A prime example of an atom economic with a recoverable catalyst is the A^3 (amine, aldehyde, alkyne) coupling with Fe_3O_4.[15] The image above shows the final step of magnetically capturing the nanoparticles with a simple bar magnet.

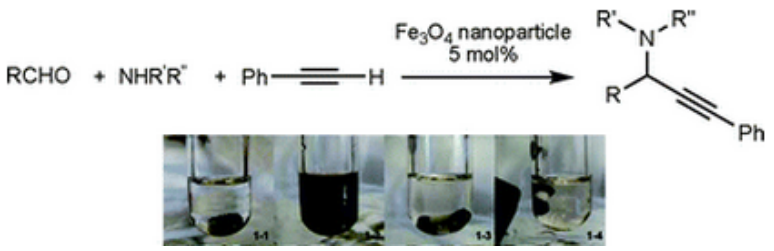


Figure 6: A3 Coupling with Iron Nanoparticle Catalysis

There are many other green chemistry techniques such as the use of supercritical CO_2, ionic liquids, water-organic interface chemistry, biocatalysis. It is up to the chemist to research alternatives for his/her syntheses rather than immediately using standard techniques.

Table 1: Savings for microscaling a reactions in undergraduate labs at Yale

Experiment	Traditional Cost	Micro Cost
Acetanilide	0.46	0.05
Aldol Condensation	5.20	0.23
Sodium Borohydride Reduction	0.16	0.02
Electrophilic Aromatic Substitution	1.01	0.02
Diphenylacetylene	0.99	.10
Tetrapheynlcyclopentadienone	2.11	0.08
Total cost per student	**$9.93**	**$0.50**

Data from 1995 Aldrich catalog

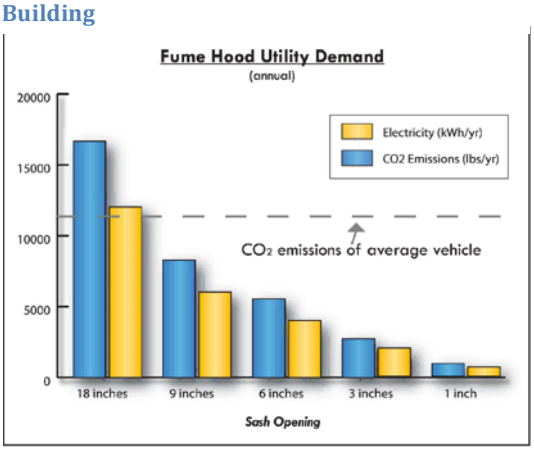
University Sustainable Research Initiatives. Many universities such have started green lab initiatives. Yale's *Environmental Health & Safety*

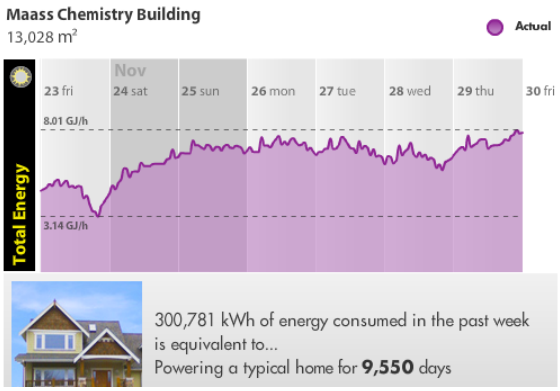
instituted microscale experiments in undergraduate research labs as part of an EPA penalty. On the right is a table demonstrating the associated chemical costs.

Both Yale and UBC recover acetone using table-top solvent recovery units, and recover silver by ion exchange chromatography.[11, 16]

Fume hoods use an average of $4,000 in energy per year, which is equivalent to 3.5 houses. [17] Universities can have over a thousand fume hoods;[17-18] an enormous opportunity to save energy lies in the behavioral change of shutting fume hood sashes when they are not in use. Energy consumption increases rapidly with sash height; UCLA reports electricity usage and CO_2 emissions in Figure 5.

Figure 7: Fume hood electricity demand and CO_2 demand at UCLA and Maas Chemistry Building





At the University of Boulder Colorado, diffusion pumps are used to reach very low-pressure vacuums for experiments in gas phase ion chemistry. They saved 58,000 kWh/yr and 1 million gallons/yr of water by installing timers to idle the pumps overnight.[19]

McGill University has had similar programs but has lots of room for improvement. The Pulse Energy program provides McGill with live weekly energy usage data by building. This can be a useful tool to monitor energy savings in the long term. The ventilation was recently reengineered to recycle heat from the fume hoods for preheating incoming outdoor air. The airflow of fume hoods is also reduced when they are not being operated.[10, 20] The implemented changes in The Otto-Maass chemistry building's are estimated to decrease its energy consumption by 60%. Other remaining challenges include overnight instrumentation power-off particular for instruments like GC-MS that are sensitive to cooling down.[10] A future challenge in green chemistry is to be able to recycle contaminated glassware. Lab supervisor, M. Huot at McGill University estimates 28 boxes of broken glassware from his lab are sent to landfill annually. [10]

Conclusion. It is evident from this research that there are many techniques already known to treat contaminated water, and reduce laboratory waste. These processes, however, can be costly and often only efficient on larger scales than a single lab. A quote by Garrigues et al.[14] summarizes the externality that is chemical waste:

"The main reason for this practice is that the economic cost of waste management is not usually paid by the analytical laboratory itself but by universities or academic authorities, so it is absolutely necessary to change the mentality of analytical chemists in this sense."

Although remediation methods are readily available the first priority is to reduce the amount of waste generated in the first place. Green Chemistry research should be coupled with policy in research institutions. For instance labs can share chemicals to prevent disposal of out of date chemicals. Chemistry labs should work with their institution to pursue efforts in green chemistry for all of their research labs in order to uphold the 12 principles of green chemistry.

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