# Health and Safety Plan

**Title:** Application of Pelletized Materials for Phosphorus Recovery
**Office:** ORD
**Laboratory:** NRMRL
**Division:** WSWRD
**Branch:** WQMB
**Building/Room:** AWBERC/B26

## Approvals

**I have read and approve the attached Health and Safety Plan in conformance with the ORD Facility Chemical Hygiene Plan and Health & Safety Plan Policy. I certify that the workplace hazards, routinely and non-routinely encountered by employees, during the described activities, and for which Personal Protective Equipment has been provided, have been assessed for the determination of Personal Protective Equipment required, in compliance with 29 CFR 1910 Subpart I.**

| | Name | Phone | Signature / Date |
|---|---|---|---|
| **Preparer** | Elisabeth Martin | (513) 569-7978 | ELISABETH MARTIN (affiliate) Digitally signed by ELISABETH MARTIN (affiliate) Date: 2016.10.04 14:44:38 -04'00' |
| **Principal Investigator** | Mallikarjuna Nadagouda | (513) 569-7232 | MALLIKARJUNA NADAGOUDA Digitally signed by MALLIKARJUNA NADAGOUDA DN: c=US, o=U.S. Government, ou=USEPA, ou=Staff, cn=MALLIKARJUNA NADAGOUDA, dnQualifier=0000036571 Date: 2016.11.29 09:48:07 -05'00' |
| **Immediate Supervisor** | Michael Elovitz | (513) 569-7642 | MICHAEL ELOVITZ Digitally signed by MICHAEL ELOVITZ Date: 2016.11.28 16:29:25 -05'00' |
| **Co-PI / Contract Manager** | | | |
| **Co-PI / Contract Manager** | | | |
| **SHEM Approval** | Steve Musson | (513)569-7969 | Musson, Steve Digitally signed by Musson, Steve DN: cn=Musson, Steve, email=Musson.Steve@epa.gov Date: 2016.11.29 13:08:35 -05'00' |

**Additional information on the completion of a Health & Safety Plan may be found at the SHEM Intranet Site.**

**Laboratory / Field Staff Concurrence**

I have read, understood and will comply with all the requirements of the attached Health and Safety Plan, SDSs, and the rules contained in the U. S. EPA- Facilities Chemical Hygiene Plan. I have also had the opportunity to ask any questions, and had my questions satisfactorily answered prior to my beginning work under this plan.

| Name (Print) | Employer (EPA, ORISE, Contractor name, etc.) | Lab (L), Field (F), or Both? | Signature | Date |
|---|---|---|---|---|
| Natalie Thompson | UC Trainee | L | | |
| Wenhu Wang | ORISE | L | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

**Project Description** *(Provide a brief synopsis/abstract of the research project. This can include background information and a general description of the research goals. Borrowing from Quality Assurance reports is acceptable and encouraged in each section of the description.)*

As the limiting nutrient in most waterways, increased loads of phosphorus can cause eutrophication, which leads to hypoxia and the proliferation of harmful algal blooms [1-3]. Additionally, while viewed as a pollutant at excessive concentrations (i.e, >20 µg L-1)[4] , phosphate, the main species of phosphorus in the environment, is necessary for a range of industrial purposes including the production of agricultural fertilizers, animal feeds, and chemical pesticides [5]. Yet phosphate reserves are quickly declining [6], making the recovery and reuse of PO43- an essential component of phosphate remediation. Adsorption is a technique which can both remove and recover PO43- from solution and has been extensively studied. However, adsorption suffers from the problem of bottle-necking (i.e., after saturation, the adsorbent will no longer be applicable) [7]. While the use of highly adsorptive fine powders which can desorb phosphate after remediation is a growing area of study [8]; their removal from solution after adsorption is difficult. Therefore, the synthesis of a highly adsorptive, inexpensive, granular sized sorbent which can recycle PO43-would be extremely beneficial to the nutrient pollution problem. Magnesium carbonate was selected to prepare pellets (i.e., 5 mm x 20 mm) as phosphate adsorbents due to its very low water solubility (i.e., 0.11 g L-1 at 25 °C) [9]. Mechanically stable pellets were prepared by blending different ratios of MgCO3 and cellulose, which acted as a binder. After pellet stability in water was ensured, the phosphate adsorption capacity of the different pellets was evaluated. Batch kinetics and isotherm studies will be conducted to evaluate the capacities as well as column breakthrough studies with more realistic water samples.

**Field Activities (if applicable) – N/A**

**Laboratory Activities (if applicable)** *(Provide a description of the laboratory activities to include methodology and processes used in the research and a description of the use of all chemicals. If referencing an SOP, please include a copy for review.)*

1. Synthesis of pellets and stock solution. Analytical grade magnesium carbonate, analytical grade calcium carbonate, and lime, will be made into pellets using the MZL Flat Die Pellet Mill from Xuzhou Orient Industry. Varying amounts of a cellulose binder, average particle size of 20 µm from Sigma Aldrich, will be used to optimize the pellet design. The phosphate stock solution will be created using 11 L of deionized water spiked with 3 g of analytical grade sodium phosphate monobasic dihydrate (NaH2PO4 ·2H2O), obtained from Fisher Scientific, and adjusted to the appropriate pH using either NaOH or HCl. A pH buffer will be used to try to maintain pH, either MOPS or TRIS.

2. Adsorption kinetics and isotherms. Preliminary batch studies will be run to assess the potential adsorption capacity of each various pellet recipe (MgCO3 + cellulose, calcined at 300°C in the Ney Vulcan A-550 oven for various times) in order to limit the number of pellets studied further through kinetics and isotherm tests. 125 mL of the sodium phosphate dihydrate stock solution will be mixed with the MgCO3 pellets and placed on a G10 Gyrotary shaker (New Brunswick Scientific Co., Inc., USA) and samples will be taken at various times to analyze for phosphate concentration. The samples will be filtered using a 0.45 µm Whatman nylon syringe filter and analyzed for phosphate using a UV-Vis

spectrophotometer (Hach DR 2700) via the USEPA PhosVer 3® (Ascorbic Acid) Method. Next, an isotherm experiment will be completed under the same conditions except with varying sorbent masses. For an isotherm, the varying mass samples will remain on the shake table for the entire equilibrium time and only one sample will be taken once equilibrium is reached. The phosphate concentration remaining in solution of each sample will be analyzed using a UV-Vis spectrophotometer (Hach DR 2700) via the USEPA PhosVer 3 (Ascorbic Acid) Method.

3. Characterization. The BET surface area will be determined using the NOVA 2000e Surface Area & Pore Size Analyzer (Quantachrome) where samples were first purged with nitrogen gas at 150°C overnight (degas) then analyzed for adsorption and desorption curves over the next day using helium with the sample tubes immersed in liquid nitrogen. Liquid nitrogen is retrieved from the Full Containment Facility and filled using a plastic tube from the tank. Cryogenic gloves are worn to remove tube and to turn off tank.

4. Column study. The chosen best pellet recipes will be placed into a column system with an influent solution spiked with 2 mM phosphate, 2mM sulfate (sodium sulfate), 2 mM nitrate (sodium nitrate) and 2 mM humic/fulvic acid and/or will be a real lake sample from Lake Harsha (QAPP # 634-Q-2-0). Various samples will be taken from the effluent tubing to analyze for the column breakthrough curve related to phosphate concentration with competing species. The samples will be analyzed using the UV-Vis spectrophotometer and the powder pillows for each species (Hach Nitraver 5 nitrate reagent, Hach Sulfaver 4 powder, Hach Phosver 3 powder pillow). Harvel plastic columns 2 ft high and 2" in diameter will be used. A stainless steel sieve is placed in the bottom of the column to prevent the media from washing out of the column. The phosphate solution will be run through the columns using a Thermo Scientific FH100M Series Peristaltic pump at a rate of 2 mL $min^{-1}$ at room temperature. The frame for the column study is already built in the lab from previous work.

5. A desorption study. A study will be conducted to evaluate how much phosphate can be recovered from the pellets after adsorption. The pellets will be placed in 125 mL of deionized water and samples taken over time to evaluate phosphate concentration.

## Physical Hazards Summary

*The physical hazards marked below have been identified as present during the performance of the project. Job hazards for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.* ***Check the Lab column for lab hazards and Field column for hazards applicable to field work.***

| Physical Hazards | Lab | Field |
|---|---|---|
| Electrical Hazards | X | |
| Radioactive Materials – requires RSO approval of HASP | | |
| Non-Ionizing Radiation | | |
| Ionizing Radiation – requires RSO approval of HASP | | |
| Heavy Lifting | | |
| Vibration | | |
| UV light/radiation | | |

| Physical Hazards | Lab | Field |
|---|---|---|
| Noise | | |
| Temperature | | |
| Illumination | | |
| Compressed Gas | | |
| Sharp Objects / Tools | | |
| Slips, Trips, Falls | | |
| Other (Specify) Rotating Machinery | X | |

**PPE Summary**

*The PPE items marked below are required to be utilized during performance of the project. PPE requirements for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.* ***Check the Lab column for lab hazards and Field column for hazards applicable to field work. *Minimum dress for entering a laboratory is closed toed shoes, long pants (waist to ankles), shirt, and safety glasses. Additional PPE shall be required based upon activities.***

| PPE Type | Lab* | Field |
|---|---|---|
| **Face / Eye Protection** | | |
| Safety Glasses w/ Side Shields | X | |
| Chemical Splash Goggles | | |
| Face Shield | | |
| Other (specify) | | |
| **Ear Protection** | | |
| Ear Plugs (Foam Inserts) | | |
| Ear Muffs | | |
| Both Ear Plugs and Ear Muffs | | |
| Other (specify) | | |
| **Hand Protection** | | |
| Nitrile disposable exam | X | |
| Latex disposable exam | | |
| Butyl disposable exam | | |
| Silver Shield® or Ansell Barrier Gloves | | |
| Thermal (Heat Resistant) Gloves | X | |
| Cryogen Gloves | | |
| Cotton Gloves | | |
| Leather Gloves | | |
| Cut Resistant (Kevlar ®) | | |
| Other (specify) | | |
| **Protective Clothing** | | |
| Lab Coat | X | |
| Lab Apron | | |
| Jumpsuit/Coveralls | | |
| Traffic Safety Vests | | |

| PPE Type | Lab* | Field |
|---|---|---|
| Shoe covers | | |
| Safety Shoes: Steel Toe Boots and Shoes | | |
| Safety Shoes: Metatarsal Boots | | |
| Safety Shoes: Slip Resistant Boots and Shoes | | |
| Oversleeves | | |
| Other (specify) | | |

**Respiratory Protection**

*Employees Wearing Respiratory Protection must be enrolled in the Respiratory Protection Program, must be medically cleared to wear a respirator, and have annual training before wearing a respirator. The respirators marked below (X) are required to be utilized during performance of the project. Respirator requirements for specific project steps are described in the Job Hazard Analysis Table at the end of the HASP.*

| | |
|---|---|
| No respirators/dust masks are required for this project. Respirator/dust mask use is not authorized. Contact the SHEM Office for requirements if respirator/dust mask use becomes necessary. | X |
| N-95 Filtering Facepiece/Dust Mask | |
| P-100 Filtering Facepiece/Dust Mask | |
| Air Purifying Half Face Respirator | |
| Air Purifying Full Face Respirator | |
| Airline Supplied Air Respirator | |
| SCBA | |
| Powered Air Purifying Respirator (PAPR) | |

**The following cartridges shall be used:**
**The cartridges shall be changed/removed from service on the following schedule:**

**Equipment Requirements**

*The safety equipment/engineering controls marked below(X) are required to be utilized during performance of the project. Requirements for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.*

| | |
|---|---|
| Chemical Fume Hood | X |
| Biological Safety Cabinet | |
| Walk-in / Bulking Hood | |
| Radiological Fume Hood | |
| Balance Enclosure | |
| Clear Air Bench (laminar flow hood) | |
| Spot Ventilation Unit (Snorkel) | |
| Local Exhaust Ventilation | |
| Canopy Hood | |
| Refrigerator / Freezer | |

| | |
|---|---|
| Deep Freezer | |
| Other (specify) | |

**Chemicals To Be Used**

*EPA utilizes an online service, Chemwatch, to provide Safety Data Sheets (SDS) to employees.*
**http://jr.chemwatch.net/chemwatch.web**
**Account: epa User Name*: Everyone* Password*: 120270.***

*If the SDS is not available through Chemwatch, a hardcopy of the manufacturer supplied SDS must be submitted to the SHEM office for upload to the Chemwatch system.* **ALL fields must be completed in the table below for all chemicals used in the project.**

| Item # | Chemical Name | CAS# | Project Use | Disposal Method for Unused Chemicals | Notes |
|---|---|---|---|---|---|
| 1 | Calcium Carbonate | 471-34-1 | Reagent | S or T | |
| 2 | Cellulose microgranular, a-Cellulose, | 9004-34-6 | Reagent | T | |
| 3 | Humic Acid | 1415-93-6 | Reagent | W | |
| 4 | MOPS | 1132-61-2 | Reagent | S or T | 2-N-morpholino]propanesulfonic acid |
| 5 | Fulvic acid | 479-66-3 | Reagent | W | |
| 6 | Hach Nitraver 5 nitrate reagent | Mixture | Reagent | W | D006. Potassium phosphate, magnesium sulfate, cadmium, gentisic acid, sulfanilic acid, copper malonate, polyacrylamide. |
| 7 | Hach Sulfaver 4 powder | mixture | Reagent | | Citric acid, barium chloride |
| 8 | Sodium Hydroxide | 1310-73-2 | Reagent | W | D002, Solution |
| 9 | Magnesium carbonate | 546-93-0 | Reagent | W | |
| 10 | TRISAMINOMETHANE ACETATE Buffer | 6850-28-8 | Reagent | W | |
| 11 | Hach Phosver 3 powder pillow | Mixture | Reagent | S or T | Potassium pyrophosphate, sodium molybdate, ascorbic acid, |

| Item # | Chemical Name | CAS# | Project Use | Disposal Method for Unused Chemicals | Notes |
|---|---|---|---|---|---|
| | | | | | Potassium Antimony Tartrate, Tetrasodium EDTA |
| 12 | Hydrochloric acid | 7647-01-0 | Reagent | W | |
| 13 | Nitrogen, liquid | 7727-37-9 | Reagent | W | |
| 14 | Sodium phosphate monobasic dihydrate | 13472-35-0 | Reagent | S or T | |
| 15 | Lime | 1305-62-0 | Reagent | W | |
| 16 | Sodium nitrate | 7631-99-4 | Reagent | W | Oxidizer-D001 |
| 17 | Sodium sulfate, anhydrous | 7757-82-6 | Reagent | S or T | |

**Biological Research** *(indicate Yes or No)*

| | |
|---|---|
| Does the project in any way involve manipulation of recombinant DNA? | No |
| If yes, are all proposed activities specifically exempted from the NIH Guidelines for Research Involving Recombinant DNA Molecules? | N/A |
| Does the project in any way involve human subjects or biological materials obtained from human subjects? | No |
| If yes, is the project exempt from the Health and Human Services Policy for Protection of Human Subjects? | N/A |
| Does the project involve animals requiring Institutional Animal Care & Use Committee (IACUC) approval? (includes vertebrate & invertebrates animals) | No |

**Biological Agents**

*The Biosafety Level (BSL) and Animal Biosafety Level (ABSL) refer to specific combinations of work practices, safety equipment, and facility design elements utilized to minimize exposure of workers and the environment to infectious agents. Principal Investigators must perform an agent risk assessment to determine the BSL. Indicate N/A if not applicable to project.*

| Item # | Biological Agent (list all that apply) | BSL # | Source of Biological Agent | Vaccination Required? |
|---|---|---|---|---|
| | None | | | |
| | | | | |
| | | | | |

**Waste Management** *(Identify process/research derived samples and wastes and indicate the intended disposal method. Hazardous Waste identification and Treatability study exemptions per 40 CFR Part 261 as reviewed in annual SHEM RCRA training.)*

The pellets after use shall be allowed to dry, bagged and trash disposed.

The leftover solution from the batch and column studies can be disposed via sink disposal.

Phosver test solutions may be sink disposed.

Nitraver tests contain cadmium. All Nitraver test solutions must be collected for disposal as hazardous waste.

Sulfaver tests contain barium. All Sulfaver test solutions must be collected for disposal as hazardous waste.

Oily rags from cleaning up oil spills from pellet make shall be collected in a plastic bag labeled "used oil" for disposal through the SHEM chemical waste program.

| | Yes | No |
|---|---|---|
| **Will Hazardous Waste Be Generated?** | X | |
| **Will the Treatability Exemption be Utilized (i.e. will materials from an outside location that would be considered hazardous waste** | | X |

**Sample Management** *(Explain how samples will be identified and labeled for storage (if not immediately discarded) and eventual disposal. Sample contents must be clearly displayed. Include storage location and how long samples must be retained.)*

All sample and reagent containers must be labeled to convey the hazards of the container. This should include all constituents including any solvent and solutes or other hazardous constituents such as contaminants within the sample/reagent container.

Any samples collected will be labeled with the date of collection, contents, and contact information. Liquid samples will only be retained until analyzed so very short term (one-two weeks). Solid samples will be stored in a cabinet labeled "Chemicals" until analysis is complete and publications are approved.

**Spill Response** *(Describe procedures for managing spills of specific hazardous chemicals, both small and large. General spills may be addressed by reference to the Chemical Hygiene Plan.)*

Spills will be handled according to the Chemical Hygiene Plan.

**The SHEM program office provides spill kits for all laboratory use. Staff should review the list and determine the location of the nearest spill kit.** *(Delete those areas not applicable)*

| | |
|---|---|
| AWBERC | G through 7 floors in the freight elevator lobby |
| AWBERC | B floor in the south wing bathroom/auditorium lobby. |

**In addition, the lab maintains spill kits in the following location: N/A**

**The biological spill kit is located: N/A**

## Authorized Personnel

Training and medical monitoring requirements will vary depending on the complexity and materials used in the process. Therefore, only personnel trained and monitored will be permitted to work under this plan. To be "authorized", employees must have completed the training and screenings selected below.

| **Mandatory for all researchers** | |
|---|---|
| **Initial Laboratory Safety** | **X** |
| **Current Chemical Hygiene Plan Laboratory Safety Refresher** | **X** |
| **Hazardous Waste Management (RCRA)** | **X** |
| | |
| **Project/Task Dependent** | |
| **Medical Surveillance** | |
| **Respiratory Protection** | |
| **Biosafety / Blood borne Pathogens** | |
| **Initial Field Safety and/or 8 hour field safety refresher training in the fiscal year** | |
| **40 - hour HAZWOPER and/or 8 hour HAZWOPER refresher in the last 12 months** | |
| **Hearing Protection** | |
| **First Aid / CPR / AED** | |
| **DOT Hazardous Materials Awareness/Shipment** | |
| **Radiation Safety** | |
| **EPA Driver's Training** | |
| **EPA Boat Safety Training** | |
| **EPA Nanomaterials Health and Safety Awareness Training** | |
| **Other (specify)** | |
| | |

**References:**

**Job Hazard Analysis, Controls, and PPE**

**Title:** Job Hazard Analysis
**Related Precautions:**

| Operation / Step | Room / Area | Potential Hazard | Recommended Action/Procedure (Engineering Controls, Prudent Practices, Safe Work Practices) | Required PPE |
|---|---|---|---|---|
| Stock solution preparation | B26 | Breathing in chemical vapors. Skin exposure. | Add acids/bases in fume hood. | Safety glasses, lab coat, nitrile gloves. |
| Making pellets | B26 | Electrical hazard, skin exposure, respiratory exposure from dust. Rotating parts. | Place cover over the machine funnel during operation to minimize dust release.<br><br>Clean dust pellet maker of all residual material after every use.<br><br>If pellet maker becomes jammed or clogged, stop operation and unplug the pellet maker before attempting to free. Do not reach with hands into operating rollers, use remote means such as spatula or other device to clear clog/jam.<br><br>Oil pellet maker before each use. Clean up all oil spills immediately and collect oily rags/towels for disposal. | Safety glasses, lab coat, nitrile gloves. |

| **Operation / Step** | **Room / Area** | **Potential Hazard** | **Recommended Action/Procedure (Engineering Controls, Prudent Practices, Safe Work Practices)** | **Required PPE** |
|---|---|---|---|---|
| Kinetics/isotherm studies/desorption. | B26 | Skin exposure. | | Safety glasses, lab coat, nitrile gloves. |
| Filling Nova 2000e liquid nitrogen dewar | FCC | See cryogenic liquid JHA in EPA Chemical Hygiene Plan. | See cryogenic liquid JHA in EPA Chemical Hygiene Plan. | Safety glasses and face shield, lab coat, cryogenic gloves. |
| Column study. | B26 | Skin exposure.<br>Splash/spray in eyes | Check all tubing and columns for damage prior to starting flow.<br>Check all tubing and columns for leaks upon starting flow and at least daily thereafter. | Safety glasses, lab coat, nitrile gloves. |
| Oven/muffle furnace use | B26 | Skin exposure. | Allow oven and items inside to cool to room temperature if possible before handling. If not, use remote handling techniques such as tongs to handle glassware. | Safety glasses, lab coat, thermal gloves. |
| Compressed Gas Use (Helium and Nitrogen) | B26 | See compressed gas JHA in EPA Chemical Hygiene Plan. | See compressed gas JHA in EPA Chemical Hygiene Plan. | Safety glasses, lab coat, nitrile gloves |

References:

[1] Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison, W. C., ... & Lewitus, A. (2008). Eutrophication and harmful algal blooms: a scientific consensus. Harmful algae, 8(1), 3-13.

[2] Paerl, H. W., Fulton, R. S., Moisander, P. H., & Dyble, J. (2001). Harmful freshwater algal blooms, with an emphasis on cyanobacteria. *The Scientific World Journal*, *1*, 76-113.

[3] Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Karl, E., ... & Gene, E. (2009). Controlling eutrophication: nitrogen and phosphorus. *Science*, *123*, 1014-1015.

[4] Correll, D. L. (1998). The role of phosphorus in the eutrophication of receiving waters: A review. *Journal of Environmental Quality*, *27*(2), 261-266.

[5] Logue, P. (1946). Industrial uses of phosphates. *J. Chem. Educ*, *23*(11), 529.

[6] Cooper, J., Lombardi, R., Boardman, D., & Carliell-Marquet, C. (2011). The future distribution and production of global phosphate rock reserves. *Resources, Conservation and Recycling*, *57,* 78-86.

[7] Lai, L., Xie, Q., Chi, L., Gu, W., & Wu, D. (2016). Adsorption of phosphate from water by easily separable Fe 3 O 4@ SiO 2 core/shell magnetic nanoparticles functionalized with hydrous lanthanum oxide. *Journal of colloid and interface science, 465*, 76-82.

[8] Rouquerol, J., Rouquerol, F., Llewellyn, P., Maurin, G., & Sing, K. S. (2013). *Adsorption by powders and porous solids: principles, methodology and applications*. Academic press.

[9] Haynes, W. M. (Ed.). (2014). *CRC handbook of chemistry and physics*. CRC press.