


5-2016

# Establishing a Vegetative Cap for Sustainable Stabilization of Copper Contaminated Soils in Torch Lake, Michigan

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ESTABLISHING A VEGETATIVE CAP FOR SUSTAINABLE STABILIZATION OF  
COPPER CONTAMINATED SOILS IN TORCH LAKE, MICHIGAN

A DISSERTATION

Submitted to the Faculty of  
Montclair State University in partial fulfillment  
of the requirements  
for the degree of Doctor of Philosophy

by

VIRINDER PAL SINGH SIDHU

Montclair State University

Upper Montclair, NJ

2016

Dissertation Chair: Dibyendu Sarkar, Ph.D., P.G.

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MONTCLAIR STATE UNIVERSITY

THE GRADUATE SCHOOL

DISSERTATION APPROVAL

We hereby approve the Dissertation

ESTABLISHING A VEGETATIVE CAP FOR SUSTAINABLE STABILIZATION OF  
COPPER CONTAMINATED SOILS IN TORCH LAKE, MICHIGAN

of

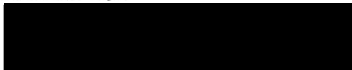
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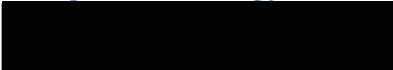
  
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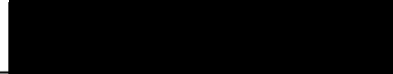
  
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## ABSTRACT

### ESTABLISHING A VEGETATIVE CAP FOR SUSTAINABLE STABILIZATION OF COPPER CONTAMINATED SOILS IN TORCH LAKE, MICHIGAN

by Virinder Pal Singh Sidhu

Extensive mining activities during the late 19<sup>th</sup> and early 20<sup>th</sup> centuries in the Upper Peninsula, Michigan have resulted in a number of contaminated sites with mine tailings. Several million metric tons of mine tailings were generated during the peak of copper (Cu) mining activities in this region. These tailings are called “stamp sands” because they were generated by crushing native Cu containing rocks, by a process known as stamping. The stamp sands were discharged into Lake Superior, other interior lakes and their shorelines, converting these areas into vast, fallow lands. The Cu contaminated stamp sands are being eroded back into the lakes, severely affecting the benthic community. The stamp sands are slightly alkaline in nature, have very low organic matter content and are highly deficient in nutrients, such as nitrogen, phosphorus and carbon. The Gay and Hubbell/Tamarack site stamp sand sites have about 50 and 19 times higher total Cu concentration compared to a normal agricultural soil, respectively. Biosolids collected from the local Portage Lake Water and Sewage Authority (PLWSA) and locally available compost was used as source of nutrients for the plants. The goal was to grow the oil seed crops camelina (*Camelina sativa*) and field pennycress (*Thlaspi arvense*) on these marginal lands, which can serve the dual purpose of producing feedstock for biofuels and reducing erosion of the Cu contaminated soils into the lakes. We conducted:

i) laboratory incubation study to evaluate the geochemical fate of copper and soil nutrient profile in contaminated stamp sands with the addition of biosolids and compost amendments, ii) greenhouse column study to evaluate the effect of compost addition and plant cover (camelina, field pennycress) on the control of stamp sand erosion and fate and distribution of Cu, iii) field simulation study to evaluate the effect of plant cover (camelina, field pennycress) on control of stamp sand erosion and to evaluate the quality of biofuels from the biofuel feedstock (camelina, field pennycress) grown in stamp sands, and iv) door to door survey of the Torch Lake Township in Upper Peninsula of MI to get the opinions of local people about starting our project of reducing stamp sand erosion and biofuel feedstock production in the Torch Lake area. Results from this study will help in the (1) development of a novel technique for the establishment of a sustainable vegetative cap to prevent erosion of stamp sands into the Torch Lake which will serve as a model for the re-vegetation of other metal-impacted areas and (2) development of a novel biodiesel feedstock production system in marginal lands using oilseed crops, which is inexpensive, sustainable and regionally-appropriate.

## ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, chair, and mentor Dr. Dibyendu Sarkar for his encouragement, understanding, support, and personal guidance, which has been vital to the overall success of my PhD research. I would also like to thank my other committee members (Drs. Datta, Deng, Butler, Solomon and Wang), who were always available to me; and without whose critique, encouragement, knowledge, and assistance this research would not have been successful. My special thanks go to Dr. Datta for permitting me to use her laboratory and greenhouse at Michigan Tech University (MTU), Houghton, Michigan. SIROM Scientific Solutions, LLC is greatly acknowledged for paid summer internships. I am also thankful to Montclair State University for the doctoral assistantship and analytical facilities. I would like to thank my family for their unending support and love. My parents and sister have always shown love and boundless inspiration from home. My wife, Rupinder offered me encouragement and moral support, particularly during my tough times as a doctoral student. I thank Portage Lake Water and Sewage Authority (PLWSA), Houghton, MI for providing the biosolids for the study. I thank USDA-NRCS for providing seeds of camelina (*Camelina sativa*) and field pennycress (*Thlaspi arvense*). I thank administration of Torch Lake Township, Upper Peninsula of MI for granting me the permission to do door to door survey and also the community of the township for participating in the survey. I thank Dr. Ramana Reddy and Jeffrey Kiiskila at MTU for their help in the collection of stamp

sands. I also thank Dr Emily Geiger at MTU for her help in the greenhouse study at MTU greenhouse.



## **DEDICATION**

*To my loving parents, Balkaur Singh Sidhu, Balvir Kaur Sidhu,*

*my sister, Kirandeep Kaur Dhaliwal*

*and*

*To my wife, Rupinder Kaur Sidhu*

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## LIST OF SYMBOLS/ABBREVIATIONS

Aluminum (Al)  
Carbon (C)  
Carbon Hydrogen Nitrogen Sulphur Analyzer (CHNS)  
Copper (Cu)  
Electrical Conductivity (EC)  
Hydrogen Ion Activity (pH)  
Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)  
Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)  
Iron (Fe)  
Michigan (MI)  
Microgram per gram ( $\mu\text{g/g}$ )  
Micro-Siemens per centimeter ( $\mu\text{S/cm}$ )  
Milligram per kilogram (mg/kg)  
Milligram per liter (mg/L)  
Nephelometric Turbidity Units (NTU)  
Nitrogen (N)  
Phosphorus (P)  
Portage Lake Water and Sewage Authority (PLWSA)  
Soil Organic Matter (SOM)  
Standard Deviation (SD)  
Total Suspended Solids (TSS)  
United States Environmental Protection Agency (USEPA)

**CHAPTER 1**

**INTRODUCTION TO RESEARCH AND ORGANIZATION OF THE**

**DISSERTATION**

**1. Introduction**

Extensive mining activities during the late 19<sup>th</sup> and early 20<sup>th</sup> centuries in Upper Peninsula, Michigan have resulted in copper (Cu) contamination of the environment. Several million metric tons of mine tailings were generated during the peak of Cu mining activities in this region. These tailings are called “stamp sands” because they were generated by crushing native Cu containing rocks via a process called stamping. The stamp sands were discharged into Lake Superior, and other interior lakes that are its offshoots. Torch Lake is part of the Keweenaw waterway in the Upper Peninsula of Michigan and connects to Lake Superior via Portage Lake. Torch Lake was filled with about 200 million tons of stamp sands from the copper industry in over a century from 1868 to 1968 filling about 20% of the lake volume (Cusack and Mihelcic 1999; Weston 2007). The mining companies dredged the sediments and dumped them on lake shores from the early to mid-1900s for copper reclamation activities converting these areas into vast, fallow lands (Weston 2007).

In 1983, the Michigan Department of Public Health (MDPH) issued a fish consumption advisory for sauger and walleye because of the high incidence of fish tumors (MDPH 1983; MDNR 1987). In 1984, the hazard ranking system was applied to

the Torch Lake site as Cu concentrations were significantly above background levels (US EPA 1989). In 1986, 14 areas within the Keweenaw Peninsula of Houghton County, Michigan were designated as a Superfund site and have been commonly referred to as the Torch Lake Superfund site (US EPA 1986). US EPA decided to establish a vegetative cover over the stamp sands surrounding the lake as part of the remediation work to delist the site (MDEQ 2007). But, the vegetation has not been able to grow uniformly over the stamp sands and there are numerous bare patches where there is no plant growth at all. Native vegetation could not grow properly because of Cu toxicity, and the nutrient-poor quality of stamp stands, which texturally lack water-holding capacity. Now, the Cu contaminated stamp sands are being eroded back into the lakes, thus affecting the aquatic population again. There were signs installed in June 2015 on Hubbell beach on the Torch Lake shoreline about potential hazards of high concentration of heavy metals in the stamp sands (TLT 2015). It is understood that unless the stamp sands are fertilized to the point of sustaining vegetation growth, the problem with erosion and water quality degradation will continue.

Biosolids are commonly used as organic fertilizers and are a sustainable and good source of nutrients, which help in the growth of plants, and also improve the soils' physical and microbiological properties (Boyl and Paul 1989; USEPA 1995; Su and Wong 2003). Biosolids can help to restore metal affected sites by providing essential nutrients to support vigorous plant cover on the mine tailings (Brown et al. 2003). Biosolids have been used to successfully restore mine lands for 25 years or more



(Haering et al. 2000; Sopper 1993). Composts have been historically used as another slow-release, organic source of fertilizer. The current incubation study was undertaken to determine if biosolids and compost amendments will be effective in providing the necessary conditions (increased nutrient content, increased organic matter) for plant growth. The establishment of plant cover on stamp sands will reduce the potential of erosion and contaminant transfer into the Torch Lake.

During the past several decades, worldwide petroleum consumption has increased tremendously due to the growth of human population and industrialization, which has resulted in depletion of fossil fuel reserves and increase in the price of petroleum. The transport sector is heavily dependent on petroleum derived fuels. Therefore, there is a great need for diesel fuel substitution all over the world with a clean, renewable fuel such as biodiesel (Balat and Balat, 2010). Biodiesel is an alternative fuel composed of mono-alkyl esters of long-chain fatty acids and is prepared from vegetable oils or animal fats by a process known as transesterification. Biodiesel has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). Biodiesel possesses significant technical advantages over petrodiesel, such as derivation from renewable feedstocks, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, superior flash point and biodegradability, reduced toxicity, as well as a reduction in exhaust emissions (Mittelbach and Remschmidt, 2004; Knothe et al., 2005; McCormick et al., 2006; Moser, 2009a). Feedstocks for biodiesel production vary considerably with location according to climate and availability. Generally, the most

abundant lipid in a particular region is the most common feedstock. Thus, rapeseed oil is predominantly used in Europe, palm oil predominates in South East Asia, and soybean oil and animal fats are primarily used in the United States, Brazil and Argentina (Mittelbach and Remschmidt, 2004; Knothe et al., 2005; Moser, 2009a). But, the high cost of commodity vegetable oils, such as soybean oil in the United States, represents a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder, 2007; Retka-Schill, 2008a). Presently, feedstock acquisition accounts for up to 85% of biodiesel production costs (Paulson and Ginder, 2007; Retka-Schill, 2008a). However, many of these oils are quite expensive and also have competing food-related uses. Consequently, the development of alternative feedstock for biodiesel production that meet all or most of the following criteria has attracted considerable research attention: high oil content, low agricultural inputs, favorable fatty acid composition, compatibility with existing farm equipment and infrastructure, production in a sustainable fashion in off-season or in agriculturally undesirable lands, definable growth seasons, and uniform seed maturation rates. Field pennycress (*Thlaspi arvense*) (Moser et al., 2009a) and camelina (*Camelina sativa*) (Moser and Vaughn, 2010) are recent examples of crops that are sources of feedstock oils for biodiesel that meet at least a majority of the above criteria.

Camelina (*Camelina sativa*) is a spring annual broadleaf oilseed member of the family Brassicaceae (Zubr, 1997). Camelina has several positive agronomic attributes: low agricultural inputs, cold-weather tolerance, short growing season (85–100 days), and it grows well in semi-arid regions and in low-fertility or saline soils. These qualities are

unusual for an oilseed crop (Putnam et al., 1993; Retka-Schill, 2008b; Sawyer, 2008). Other oilseed crops, such as canola, soybean, rapeseed, and sunflower, have higher water, pesticide, and fertilizer requirements (Budin et al., 1995; Sawyer, 2008). Moreover, camelina, unlike soybean, thrives in cool, arid climates and is nicely adapted to the more northerly regions of North America, Europe, and Asia. Camelina can be grown on marginal land and has low water and fertilizer requirement becoming a low-input biofuel crop (Vollmann et al., 1996).

Field pennycress (*Thlaspi arvense*) is a winter annual belonging to the Brassicaceae family. It is native to Eurasia but has an extensive distribution throughout temperate North America. Field pennycress is highly adapted to a wide variety of climatic conditions (Lu and Kang, 2008). It is generally considered to be an agricultural pest or a weed. Field pennycress can grow on marginal lands, requires minimal agricultural inputs (fertilizer, pesticides, water), and is not part of the food chain (Dolya et al., 1976; Marek et al., 2008; Moser et al., 2009; Zubr, 1997). Although, field pennycress seed meal cannot be used as an animal feed because of high glucosinolate content, but other applications such as biofumigation have been reported (Lu and Kang, 2008).

The oil content of Camelina has more than 40% polyunsaturated fatty acids in which linolenic acid makes up about 35% in addition to omega-3 fatty acids (Gebauer et al., 2006). Historically, camelina has been cultivated for oil in Europe, Central Asia and

North America. Presently, camelina is being grown to produce aviation biofuels. Japan Airline, Air New Zealand and the US Navy (F/A18) have successfully completed test flights with a 50/50 blend of camelina based biofuel and petroleum based jet fuel. Camelina yields an average of 420–640 L/ha and the protein and fiber content in its meal byproduct is comparable to that of soybean meal (Retka-Schill, 2008b).

Field pennycress has high oil content (20-36 %) (Dolya et al., 1976; Marek et al., 2008; Moser et al., 2009; Zubr, 1997). Additionally, each plant can produce up to 15,000 seeds and yield from wild populations is in the range of 1120-2240 kg of seed/ha, which can generate about 600-1200 L of oil/ha versus 450 L/ha in case of soybean (Marek et al., 2008). This common roadside plant can become a new source of biofuel (USDA, 2010). Scientists working in the Agricultural Research Service (ARS), USDA's principal scientific research agency, have found that impressive quantities of seeds produced by field pennycress can yield oil that can be used in biodiesel production (USDA, 2010).

My long-term goal was to develop a novel, low cost and sustainable technique to grow oil seed crops (camelina and field pennycress) on the stamp sands in the Torch Lake area of Michigan's Upper Peninsula. The results from this project will have a broader impact of demonstrating an effective low-cost, environment friendly technology to help alleviate the erosion of stamp sands in those regions of the Torch Lake area of concern (AOC) which lack a vegetative cap.

## **1.1 Research Objectives**

The first objective of the study was to evaluate the geochemical fate of copper and soil nutrient profile in contaminated stamp sands with the addition of biosolids and compost amendments.

The second objective of the study was to evaluate the effect of compost addition and plant cover (camelina, field pennycress) on the control of stamp sand erosion and fate and distribution of copper in a greenhouse column study.

The third objective of the study was to evaluate the effect of plant cover (camelina, field pennycress) on the control of stamp sand erosion in a field simulation study and to evaluate the quality of biofuels from the biofuel feedstock (camelina, field pennycress) grown in stamp sands.

The fourth objective of the study was to get the opinions of local people about starting our project of reducing stamp sand erosion and biofuel feedstock production in the Torch Lake area by conducting a door to door survey of the Torch Lake Township.

## **1.2 Organization of the dissertation**

The above mentioned research objectives were achieved and research findings were organized in the form of various chapters in this dissertation. Each chapter covers one research objective as follows:

- Chapter 2 entitled, “Effects of biosolids and compost amendment on chemistry of soils contaminated with copper from mining activities: An incubation study”,

evaluated the effects of locally available biosolids and compost addition on the soil nutrient profile of stamp sands, and organic matter content in a 2-month long incubation experiment. The study also investigated effects of such organic fertilizer amendments on geochemical speciation of copper in the stamp sands at 0, 30 and 60 days.

- Chapter 3 entitled, “Effect of compost addition and plant cover on the erosion control of contaminated stamp sands and fate and distribution of copper in the stamp sands: Greenhouse and field simulation studies”, assessed the effects of compost amendment and plant cover [camelina (*Camelina sativa*) and field pennycress (*Thlaspi arvense*)] in controlling stamp sand erosion in a greenhouse column experiment and a follow up field simulation experiment in a greenhouse. The study also evaluated the effects of compost addition and plant cover on the fate and distribution of copper in the contaminated stamp sands. The study also assessed the biofuel quality from the biofuel feedstock (camelina).
- Chapter 4 entitled, “Effect of the reduction in stamp sand erosion and biofuel feedstock production on the local community in Torch Lake, MI: A door to door survey”, assessed the opinions of the community in Torch Lake Township about initiating our project involving reduction of stamp sand erosion and biofuel feedstock (camelina and field pennycress) production in Torch Lake area, MI by conducting a door to door survey. The residents of Torch Lake Township in the

Upper Peninsula of Michigan were asked questions via a questionnaire about growing biofuel feedstock crops on stamp sands near their township.

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## CHAPTER 2

### **EFFECT OF BIOSOLIDS AND COMPOST AMENDMENT ON CHEMISTRY OF SOILS CONTAMINATED WITH COPPER FROM MINING ACTIVITIES: AN INCUBATION STUDY**

(A portion of this chapter has been accepted in the journal, Environmental Monitoring and Assessment)

#### **Abstract**

Several million metric tons of mining wastes, called stamp sands were generated in the Upper Peninsula of Michigan during extensive copper (Cu) mining activities in the past. These materials, containing large amounts of Cu, were discharged into various offshoots of Lake Superior. Due to evidences of Cu toxicity on aquatic organisms, in due course, the materials were dredged and dumped on lake shores, thus converting these areas into vast, fallow lands. Erosion of these Cu-contaminated stamp sands back to the lakes is severely affecting aquatic life. Lack of uniform vegetation cover on stamp sands is facilitating this erosion. Understanding the fact that unless the stamp sands are fertilized to the point of sustaining vegetation growth, the problem with erosion and water quality degradation will continue, amending the stamp sands with locally available biosolids and composts were considered. The purpose of the reported study was to assess potential effects of such organic fertilizer amendments on soil quality. As the first step of

a combined laboratory and greenhouse study, a 2-month long incubation experiment was performed to investigate the effects of biosolids and compost addition on the soil nutrient profile of stamp sands, and organic matter content. Results showed that both biosolids and compost amendments resulted in significant increase in nitrogen and phosphorus concentrations and organic matter contents of stamp sands. Sequential extraction data demonstrated that Cu was mostly present as bound forms in stamp sands, and there was no significant increase in the plant-available fraction of Cu because of fertilizer application.

Key words: Mining, copper contamination, stamp sands, biosolids, compost, soil quality

## **2. Introduction**

Extensive mining activities during the late 19<sup>th</sup> and early 20<sup>th</sup> centuries in Upper Peninsula, Michigan have resulted in copper (Cu) contamination of the environment. Several million metric tons of mine tailings were generated during the peak of Cu mining activities in this region. These tailings are called “stamp sands” because they were generated by crushing native Cu containing rocks via a process called stamping. The stamp sands were discharged into Lake Superior, and other interior lakes that are its offshoots. Torch Lake is part of the Keweenaw waterway in the Upper Peninsula of Michigan and connects to Lake Superior via Portage Lake. The lake was filled with about 200 million tons of stamp sands from the copper industry in over a century from 1868 to 1968 filling about 20% of lake volume (Cusack and Mihelcic 1999; Weston 2007). The

mining companies dredged the sediments and dumped them on lake shores from early to mid-1900s for copper reclamation activities converting these areas into vast, fallow lands (Weston 2007). In 1983, the Michigan Department of Public Health (MDPH) issued a fish consumption advisory for sauger and walleye because of the high incidence of fish tumors (MDPH 1983; MDNR 2007). In 1984, the hazard ranking system was applied to the Torch Lake site as Cu concentrations were significantly above background levels (US EPA 1989). In 1986, 14 areas within the Keweenaw Peninsula of Houghton County, Michigan were designated as a Superfund site and were commonly referred to as the Torch Lake Superfund site (US EPA 1986). US EPA decided to establish a vegetative cover over the stamp sands surrounding the lake as part of the remediation work to delist the site (MDEQ 2007). But, the vegetation has not been able to grow uniformly over the stamp sands and there are numerous bare patches where there is no plant growth at all. Native vegetation could not grow properly because of Cu toxicity, and the nutrient-poor quality of stamp stands, which texturally lack water-holding capacity.

Now, the Cu contaminated stamp sands are being eroded back into the lakes, thus affecting the aquatic population again. There are signs installed in June 2015 on Hubbell beach on the Torch Lake shoreline about potential hazards of high concentration of heavy metals in the stamp sands (TLT 2015). It is understood that unless the stamp sands are fertilized to the point of sustaining vegetation growth, the problem with erosion and water quality degradation will continue.

Biosolids are commonly used as organic fertilizers and are a sustainable and good source of nutrients, which help in the growth of plants, and also improve the soils' physical and microbiological properties (Boyl and Paul 1989; USEPA 1995; Su and Wong 2003). Biosolids can serve to restore metal affected sites by providing essential nutrients to support vigorous plant cover on the mine tailings (Brown et al. 2003). Biosolids have been used to successfully restore mine lands for 25 years or more (Haering et al. 2000; Sopper 1993). Composts have been historically used as another slow-release, organic source of fertilizer. The current incubation study was undertaken to determine if biosolids and compost amendments will be effective in providing the necessary conditions (increased nutrient content, increased organic matter) for plant growth. The establishment of plant cover on stamp sands will reduce the potential of erosion and contaminant transfer into the Torch Lake. We also wanted to investigate the effects of biosolids and compost addition on the geochemical fate of copper in stamp sands. Specifically, we wanted to know if the organic amendments are further solubilizing Cu, thus making it more available for plant uptake and leaching.

The objectives of the present incubation study were:

1. To assess the effects of biosolids and compost on nutrient content and organic matter of stamp sands.
2. To assess the effects of biosolids and compost on the geochemical forms of Cu in stamp sands.

## **2.1 Materials and Methods**

### ***2.1.1 Soil sampling, preparation and characterization***

Stamp sand was collected from Hubbell/Tamarack site near Torch Lake, Upper Peninsula of Michigan. The physical and chemical properties of stamp sands are listed in Table 1. Air-dried and sieved (2 mm) soil was used for the determination of pH, electrical conductivity (EC), soil moisture and organic matter content using standard protocols (Sparks 1996). Available P was extracted by Mehlich III solution (Mehlich 1984). Total Cu, Fe, Al and P was determined by acid digestion according to the USEPA Method 3050B (USEPA 1996). The acid digests were analyzed in Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). The soil particle size distribution was determined by the pipette method (Gee and Bauder 1986).

### ***2.1.2. Soil amendments***

Biosolids were obtained from Portage Lake Water and Sewage Authority (PLWSA), Houghton, MI. Compost was bought from a local nursery. Biosolids and composts were added at rates of 0, 25 g/kg (2.5%), 50 g/kg (5%), 100 g/kg (10%) and 200 g/kg (20% stamp sand and incubated in polyethylene bags at 70% water holding capacity. Soil samples were collected on 0, 15, 30 and 60 days and analyzed for pH, EC (Sparks 1996), organic matter (Schulte and Hopkins 1996), total carbon, total nitrogen (Nelson and Sommers 1982), total phosphorus (USEPA 1996), plant available phosphorus (Mehlich 1984) and sequential extraction of Cu at 0, 30 and 60 days



(Tessier et al 1979).

### ***2.1.3. Organic Matter, Carbon and Nitrogen Analysis***

Organic matter content was measured in the samples by loss on ignition method (Schulte and Hopkins 1996). The samples were weighed (3 g) in crucibles and kept in a hot air oven at 105°C for 24 hours. After oven drying the samples, the samples were weighed again to account for soil moisture, then kept in the muffle furnace and maintained at 360°C for 2 hours. The samples were cooled and weighed to observe the loss in weight which accounted for soil organic matter (Schulte and Hopkins 1996). Total C and total N were measured in samples using a Perkin-Elmer 2400 CHN analyzer (Nelson and Sommers 1982). 10-20 mg of oven dried soil samples were weighed and wrapped in aluminum foil and analyzed for total C and total N in the CHNS analyzer (Nelson and Sommers 1982).

### ***2.1.4. Sequential Extraction Procedure***

Soil samples collected on 0, 30 and 60 days were sequentially extracted for determination of geochemical forms of Cu. Sequential extraction of Cu was performed using the procedure reported by Tessier et al. (1979) for the following operationally defined forms: (1) water soluble phase, (2) exchangeable phase, (3) carbonate bound phase (4) Fe and Al bound phase and (5) organic bound phase (6) residual bound phase. One gram oven dried soil from each treatment was diluted with 15 mL deionized water in a 50 mL tube and shaken on an orbital shaker at 250 revolutions per minutes (rpm) for 2

hours. The solutions were then centrifuged at 3500 revolutions per minutes (rpm) for 30 minutes. The supernatants were collected in separate 50 mL tubes, filtered and analyzed for water soluble Cu using ICP-MS. The residue from water soluble fraction was extracted at room temperature for one hour with 8 mL of 1M MgCl<sub>2</sub> for exchangeable fraction. The residue from the exchangeable was extracted with 8 mL of 1 M CH<sub>3</sub>COONa (adjusted to pH 5.0 with CH<sub>3</sub>COOH) for 5 hours for carbonate bound fraction. The residue from carbonate fraction was extracted at 96<sup>0</sup>C for 6 hours with 3 mL of 0.04 M NH<sub>2</sub>OH.HCl in 25% (v/v) CH<sub>3</sub>COOH for oxides of aluminum (Al) and iron (Fe) bound fraction. The residue from Al and Fe oxides bound fraction was extracted with 3 mL of 0.02 M HNO<sub>3</sub> and 8 mL of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0 with HNO<sub>3</sub>) at 85<sup>0</sup>C for 5 hours. After cooling, 5 mL of 3.2 M CH<sub>3</sub>COONH<sub>4</sub> was added in 20% (v/v) HNO<sub>3</sub>. This step extracted organic bound fraction. The residue from organic bound fraction was extracted with 25 mL concentrated HNO<sub>3</sub> at 105<sup>0</sup>C, and digested until 5 mL was left in the beaker. This step extracted the residual bound fraction of Cu. All treatments were carried out in triplicates and the respective solutions were centrifuged at 3500 x g for 30 minutes. The supernatants were collected in separate 50 mL tubes, filtered and analyzed for Cu using ICP-MS.

#### ***2.1.5. Statistical analysis***

The data were statistically analyzed using the statistical software JMP version 10 (SAS 2012). Means were compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ) to test for significant difference among different levels of biosolids and compost.

## 2.2 Results and discussion

### 2.2.1. Properties of Soil and Amendments

Properties of the stamp sands, biosolids, and compost are given in Table 2-1. The stamp sands were slightly alkaline (8.2) in nature. Biosolids had a slightly acidic pH (6.0) and compost had a near neutral pH (6.9). The stamp sands had an electrical conductivity (EC) of 83  $\mu\text{S}/\text{cm}$ , which was expected given its very sandy texture, and very low water/salt holding capacity, whereas biosolids and compost had EC of 1375 and 1840  $\mu\text{S}/\text{cm}$ , respectively. Stamp sands had an organic matter content of 0.5 % whereas biosolids and compost had organic matter contents of 58 and 84 %, respectively.

Table 2-1: Properties of soil, biosolids and compost

Properties	Stamp sand	Biosolids	Compost
pH	8.2	6.0	6.9
EC <sup>a</sup> ( $\mu\text{S}/\text{cm}$ )	83	1375	1840
SOM <sup>b</sup> (%)	0.5	58	84
Sand (%)	95	-	-
Silt (%)	2.5	-	-
Clay (%)	2.5	-	-
Cu (mg/kg)	719	709	54
Fe (mg/kg)	6200	27710	-
Al (mg/kg)	2300	1180	-
Plant Available P (mg/kg)	0.70	9100	1009
Total P (mg/kg)	800	28560	2090
Total N (g/kg)	1.81	266	388

<sup>a</sup> EC = electrical conductivity

<sup>b</sup> SOM = soil organic matter

The stamp sands, as the name implies, were sandy in texture with 95% sand, and 2.5% each of silt and clay. The Cu concentration in stamp sands, biosolids and compost

was 719, 709 and 54 mg/kg, respectively. Biosolids had almost the same Cu content as the stamp sands, which made its choice as a fertilizer amendment dubious. The concentrations of total iron (Fe) and aluminum (Al) in stamp sands were 6200 and 2300 mg/kg, respectively. Biosolids had Fe and Al concentration as 27,710 and 1180 mg/kg, respectively. Stamp sands had a total and plant available phosphorus (P) content of 800 and 0.7 mg/kg, respectively. Biosolids had a total and plant available P content of 28,560 and 9100 mg/kg, respectively. Compost had a total and plant available P as 2090 and 1009 mg/kg, respectively. The nitrogen (N) content in stamp sands, biosolids and compost was 1.81, 266 and 388 g/kg, respectively. The remediation work done by US EPA on the Torch Lake superfund site in 2005 (MDEQ 2007) may have increased the total P content of stamp sands. But, as evidenced from the Mehlich 3 results (Table 1), a very small fraction of that total P is plant available (less than 0.1%); rest of the P in stamp sands is in bound forms, and not available to plants.

### ***2.2.2. Effect of soil amendments on pH***

The pH of biosolids amended stamp sands decreased significantly at higher rates of biosolids application (10 and 20%) (Fig. 2-1). This was due to the acidic pH of the biosolids (5.95). In case of compost amendment, the pH of the stamp sands remained above 7.0 over the 60 day period, regardless of the rate of application (Fig. 2-2). In general, compost amendment resulted in lowering the pH of native stamp sands to a more healthy level.

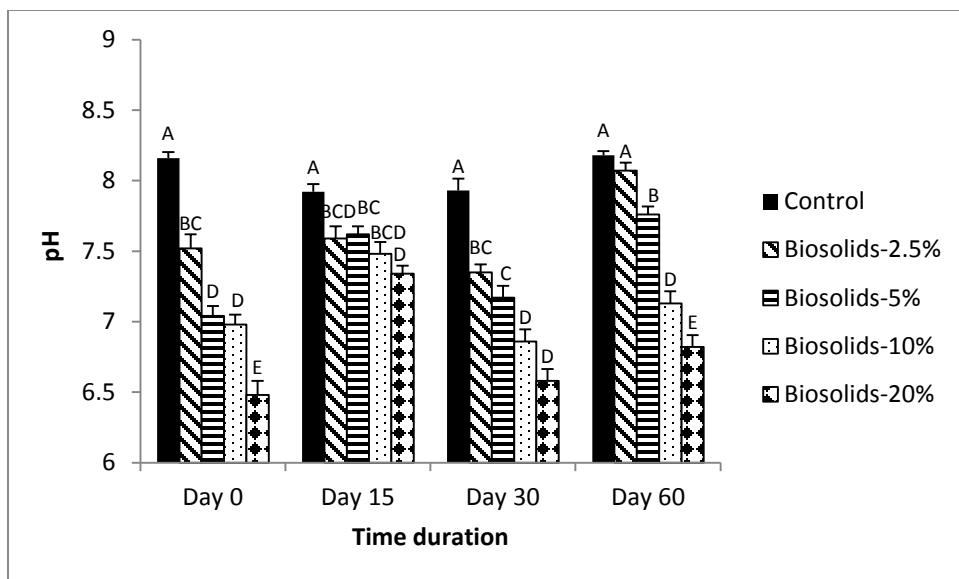


Fig. 2-1: pH of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

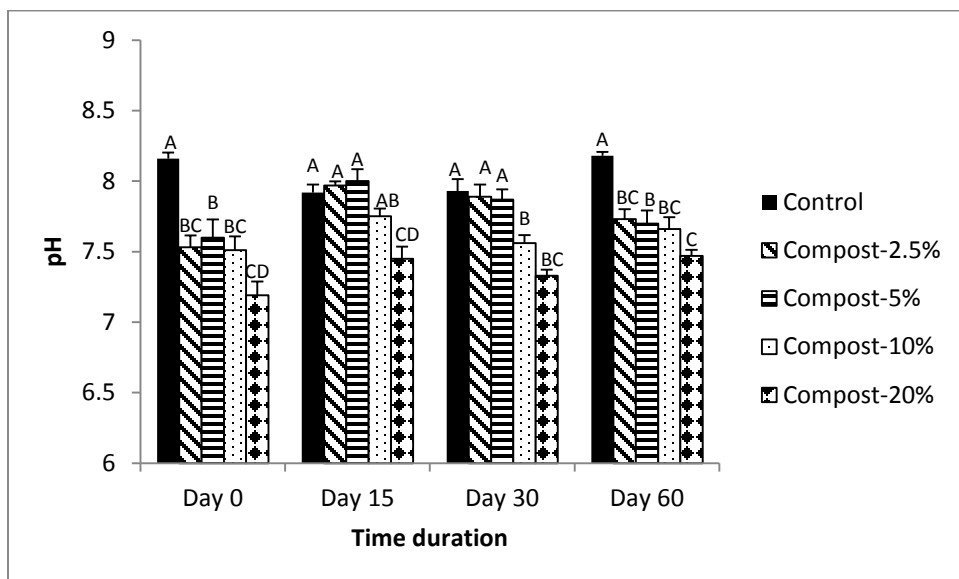


Fig. 2-2: pH of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

However, the pH changes were not statistically different, except for the highest rate of compost amendment (20%), where the pH was significantly different relative to the control.

### ***2.2.3. Effect of soil amendments on electrical conductivity***

As expected, the EC of the biosolids amended stamp sands increased significantly at all rates of biosolids application during the incubation study period because of the increased amount of salt added by the biosolids to the salt-deficient native soil. The increase in EC was about 27 times in 20% biosolids amendment rate compared to the control (Fig. 2-3).

Similar trend was noticed in case of compost amendment, with significant increases in EC in the 10% and 20% compost amendment rates (Fig. 2-4). The increase in EC was much lower in compost amended soils compared to biosolids amendment. For example, the increase in EC was about 8 times in 20% compost amendment rate compared to the control. Eghball (2002) also observed that soil EC increased with increasing rate of compost application.

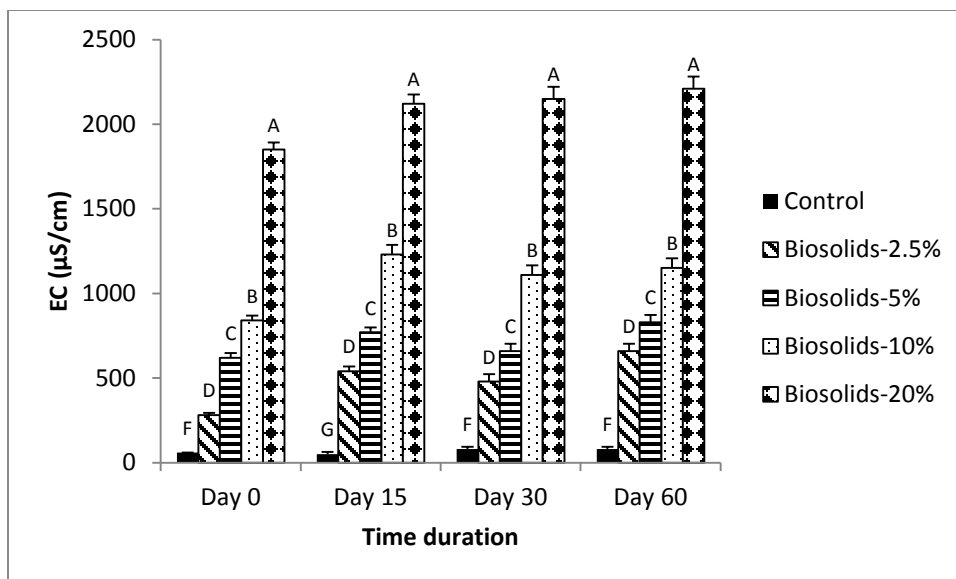


Fig. 2-3: Electrical Conductivity (EC) ( $\mu\text{S}/\text{cm}$ ) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

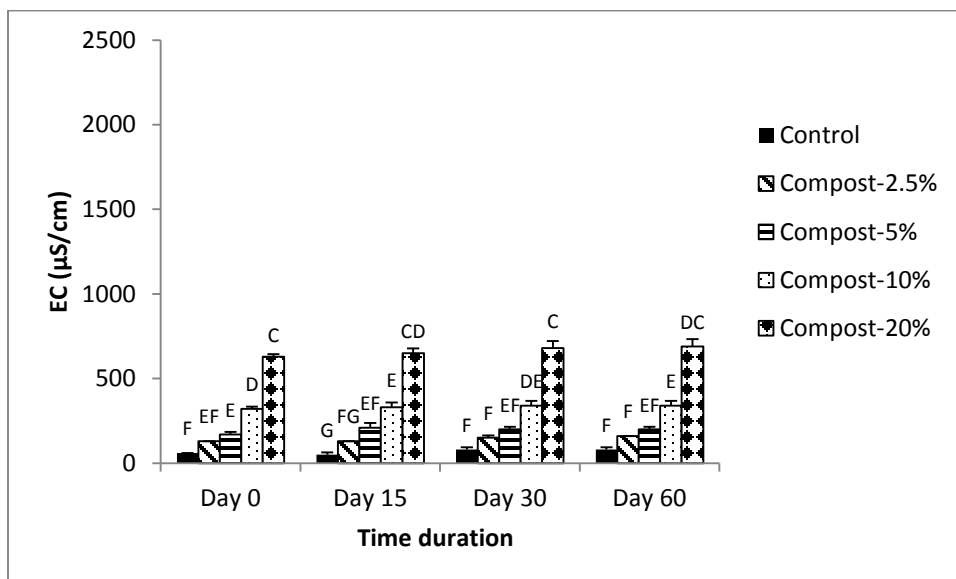


Fig. 2-4: Electrical Conductivity (EC) ( $\mu\text{S}/\text{cm}$ ) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

#### 2.2.4. Effect of soil amendments on nutrient contents (nitrogen, phosphorus and carbon)

The stamp sands were nutrient deficient (Table 2-1), one of the reasons it is so difficult to establish a vegetation cap. The remediation work done by US EPA on the Torch Lake superfund site in 2005 (MDEQ 2007) may have increased the P content of stamp sands, but a very small percentage of total P is plant available (Table 2-1). The rest of total P is in bound forms and not available to plants. The N concentration of biosolids amended stamp sands increased significantly at all rates of biosolids application (Fig. 2-5).

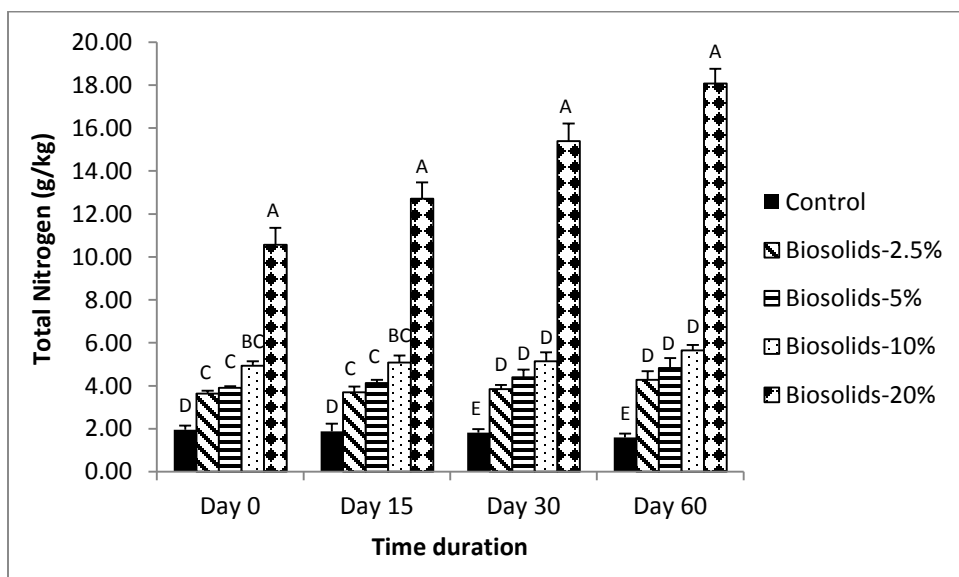


Fig. 2-5: N content (g/kg) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.



The increase was almost 9 times compared to control at the highest rate of biosolids (20%) application at the end of the study. Similarly, in case of compost amendment, there was significant increase in N in stamp sands at all rates of compost amendment. At the end of the study period, compost amendment at a rate of 20% lead to a seven fold increase in N concentration (Fig. 2-6).

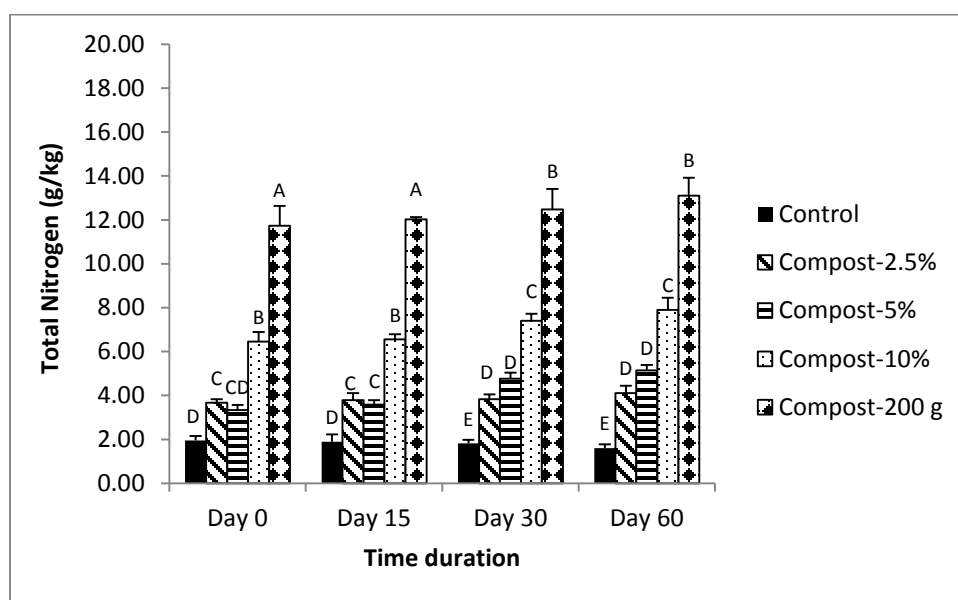


Fig. 2-6: N content (g/kg) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

The maximum agronomical recommended N application rate for Michigan is 1210 kg/ha (Vitosh et al. 1995). Assuming all N to be plant available, the biosolids and compost amendments increased the N content of stamp sands beyond the maximum agronomical-recommended N at the highest application rate.

The concentration of total P in stamp sands increased significantly with 10 and 20% biosolids amendment during the 60 day study period (Fig. 2-7). In case of biosolids amendment at higher rates, especially at 20%, total P increased at day 15 and then decreased to 1501 mg/kg.

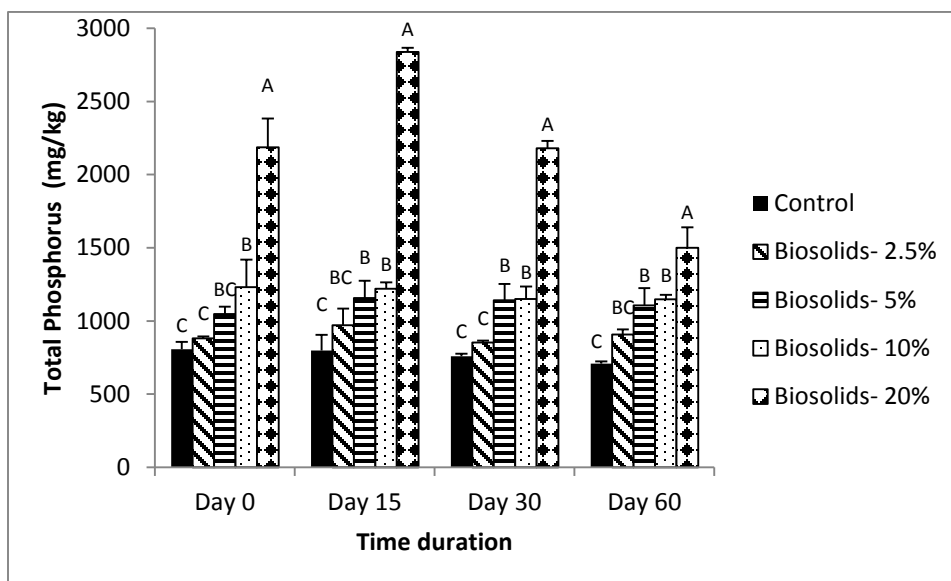


Fig. 2-7: Total P content (mg/kg) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

In case of compost amendment, there was a significant increase in total P at the 20% rate by the end of the study period (Fig. 2-8). The plant available P content of stamp sand significantly increased at higher rates (10 and 20%) of biosolids (Fig. 2-9) and compost (Fig. 2-10) amendment by the end of study period. The maximum values of plant available P in both biosolids and compost amended stamp sand (26.7 and 24.6

mg/kg, corresponding to 48.1 and 44.3 kg/ha, respectively) were well below the maximum agronomical recommended P application rate (1018 kg/ha) for Michigan (Vitosh et al. 1995), indicating that these rates of fertilizer amendment are unlikely to cause eutrophication.

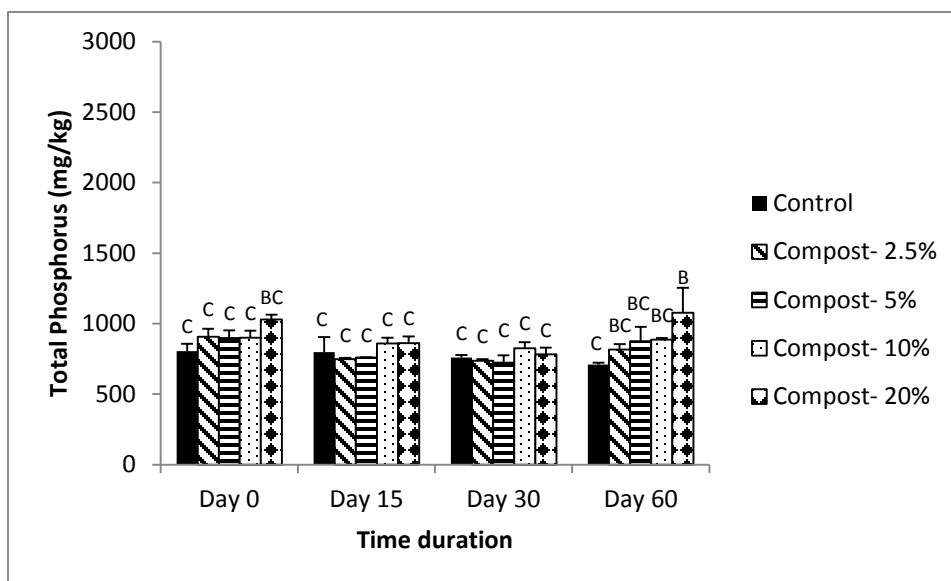


Fig. 2-8: Total P content (mg/kg) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

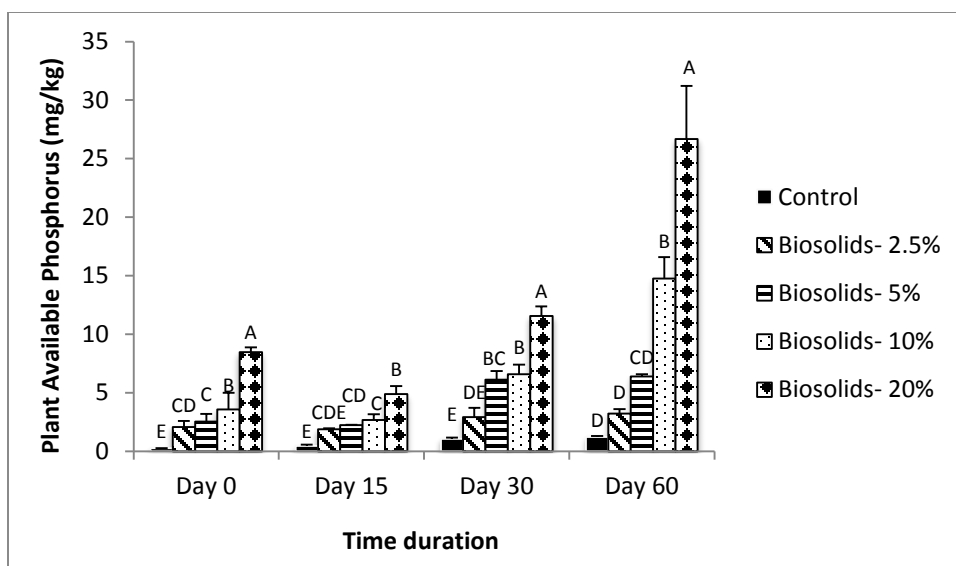


Fig. 2-9: Plant available P content (mg/kg) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

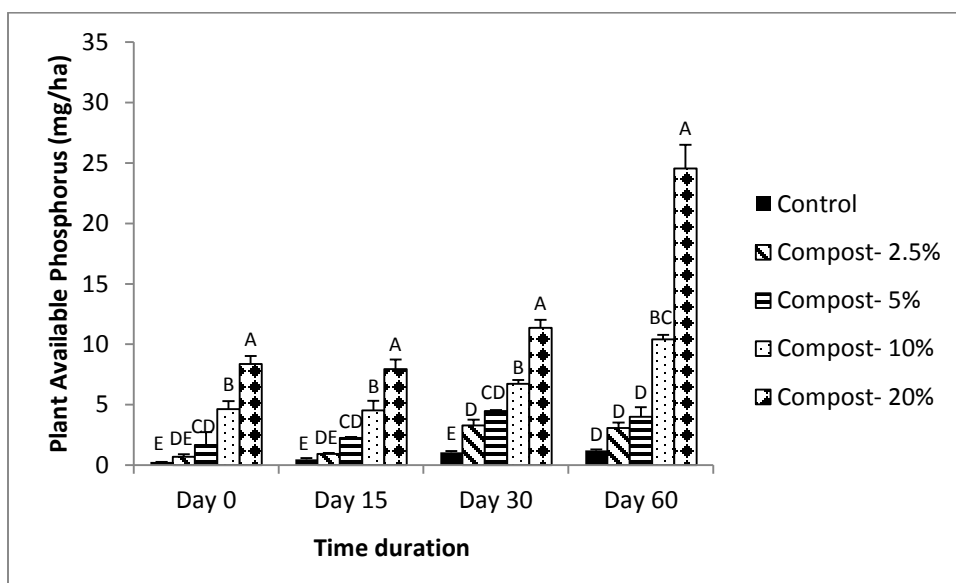


Fig. 2-10: Plant available P content (mg/kg) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Shober et al. (2003) and Maguire et al. (2000) also found significant increase in soil P where biosolids were applied. Shober et al. (2003) did not find any increase in soil P below 10 cm depth; Maguire et al. (2003) observed the highest concentration of P in the top 5 cm layer of soil, indicating no leaching. There is very little chance of leaching of any plant available P due to the presence of high concentrations of Al and Fe oxides in the biosolids (Elliott et al. 2002; O'Connor and Sarkar 2000), and in stamp sands.

The carbon (C) content of the biosolids amended stamp sands increased significantly at 10 and 20% of biosolids application. The increase was about 1.5 times control at the highest rate of biosolids (20%) at the end of the study (Fig. 2-11).

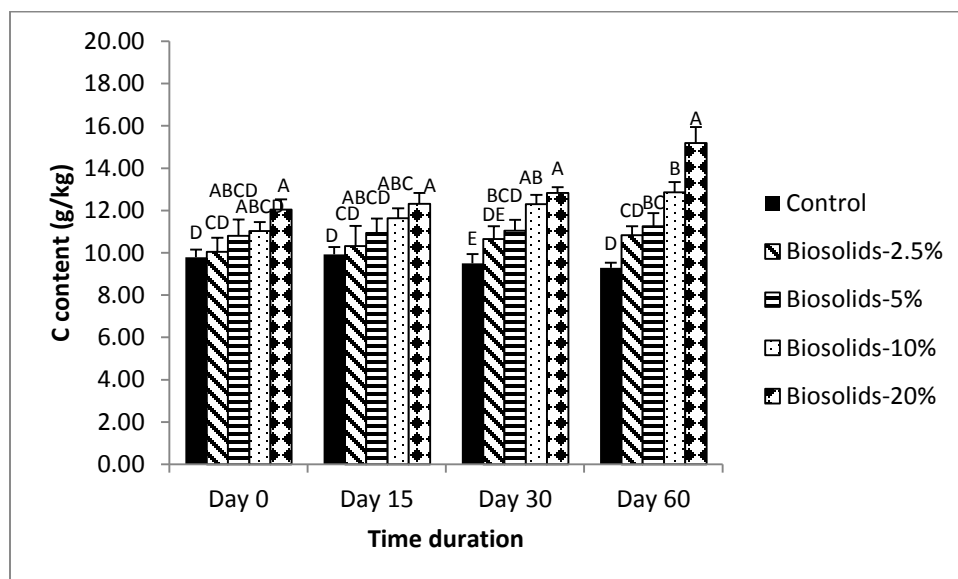


Fig. 2-11: C content (g/kg) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

In case of compost amendment, the increase in C contents followed the same trend as in case of biosolids amendment (Fig. 2-12). Deboz et al. (2002) also observed an increase in soil carbon due to application of biosolids and compost in an incubation study.

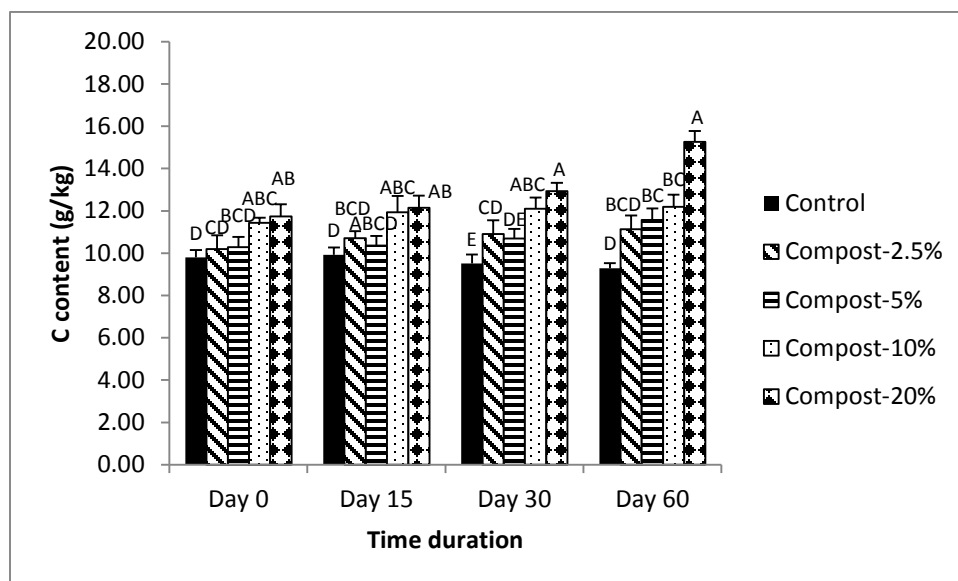


Fig. 2-12: C content (g/kg) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 2.2.5. Effect of soil amendments on organic matter

The organic matter content of biosolids amended stamp sands increased significantly at all rates of biosolids application from day 15. The increase was close to 2.5% at the highest rate of biosolids amendment by the end of the study (Fig. 2-13).

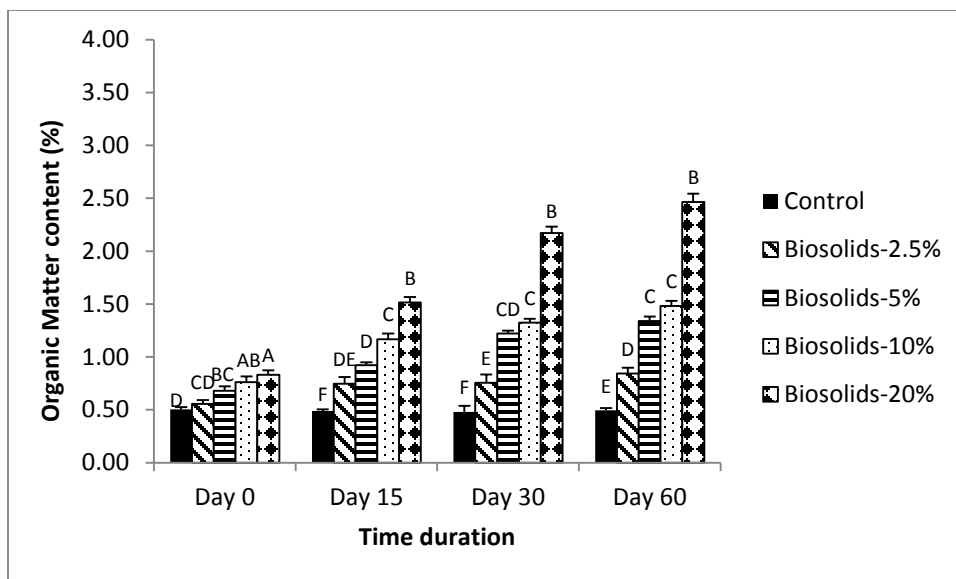


Fig. 2-13: Organic matter contents (%) of stamp sand as affected by different rates of biosolids during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

In case of compost amendment, the increase in organic matter was more than biosolids, with a maximum increase of 3.7% (compost 20%; Fig. 2-14). Rivero et al. (2004) conducted a field study where compost was applied annually for three years to the field plots. They found that addition of compost not only increased the quantity of soil organic matter in the soil, but also increased the quantity of humic acid with more functional groups and aromaticity, thus improving soil quality and productivity. Moffet et al. (2005) and Tian et al. (2009) found that application of biosolids increased the soil organic matter content of soils.

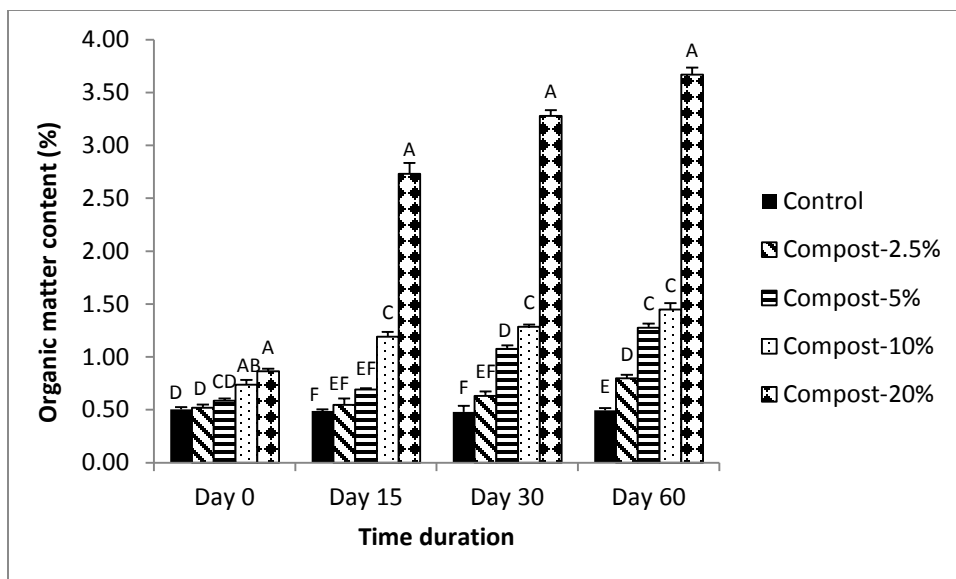


Fig. 2-14: Organic matter contents (%) of stamp sand as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 2.2.6. Geochemical forms of Cu

In terms of water soluble fraction (F1), there was not much change in Cu concentration in stamp sands amended with biosolids (Table 2-2) and compost (Table 2-3) during the entire 60-days incubation study period. The percentage of water soluble Cu stayed below 1.5% and 1.0% in the water soluble fraction across the amendment rates of biosolids and compost, respectively. In the exchangeable Cu fraction (F2), there was a slight increase in after day 30 in case of biosolids and compost amendments, but it remained below 4% across all rates. Moreover, this increase in exchangeable Cu percentage was also observed in the control treatment that received no fertilizer



treatment. Hence, the impact of organic fertilizer amendment on plant available (soluble plus exchangeable) fraction of Cu can be considered negligible. However, given that biosolids had a high concentration of Cu (709 mg/kg; Table 2-1), the addition of biosolids to stamp sands increased total Cu concentrations as a function of amendment rate (18, 36, 71 and 142 mg Cu/kg stamp sand from 2.5, 5, 10 and 20% biosolids rate, respectively).

Table 2-2: Percent (%) Cu in each fraction as influenced by different rates of biosolids over the incubation study period

Rate of biosolids	Time period	F1	F2	F3	F4	F5	F6
Control	Day 0	0.54	0.06	16.9	34.9	31.0	16.6
	Day 30	0.40	2.57	11.4	48.5	20.4	16.7
	Day 60	0.30	3.81	16.1	29.0	27.6	23.2
Biosolids-2.5%	Day 0	0.41	1.01	13.2	29.1	48.3	7.96
	Day 30	0.51	1.92	19.2	40.6	20.0	17.9
	Day 60	0.32	3.63	18.5	24.5	29.9	23.1
Biosolids-5%	Day 0	0.54	2.06	14.9	8.80	59.1	14.6
	Day 30	0.65	1.12	18.2	41.1	21.4	17.6
	Day 60	0.40	3.26	15.8	30.9	27.3	22.4
Biosolids-10%	Day 0	0.87	2.94	12.5	4.50	59.9	19.2
	Day 30	0.95	1.06	11.8	39.6	26.2	20.5
	Day 60	0.55	3.46	12.6	26.1	35.2	22.2
Biosolids-20%	Day 0	1.08	2.80	4.98	2.32	73.7	15.1
	Day 30	1.36	1.04	9.59	28.2	34.4	25.4
	Day 60	0.75	3.20	13.5	15.3	39.3	27.9

More than 95% of Cu was bound to various soil components (fractions F3, F4, F5, and F6) regardless of the source of fertilizer or amendment rate. At the end of the 60-day incubation period, the highest percentage of Cu in carbonate bound fraction (F3) in

the biosolids and compost amended stamp sands remained below 30%. In terms of Al and Fe oxides-bound fraction (F4), Cu concentration increased at the end of the study compared to day zero at all rates except for the control, and 2.5% biosolids treatment. In terms of organic bound fraction (F5), the highest rate of biosolids (39.3%) and compost addition (48.4%) resulted in the highest Cu concentrations. There was an increase in Cu concentration in the residual bound fraction (F6) with increasing rate of biosolids and compost amendments, except in the 5% compost rate. At day 60, Cu concentrations in the residual bound fractions were reflective of amendment rates of biosolids and composts (27.9% and 32%, respectively at the highest amendment rate).

Our findings were similar to those of Guerra et al. (2007) who reported that Cu was primarily distributed in soil in the residual, iron oxides, carbonate and organic bound fractions, and was not significantly available for plant uptake after biosolids amendment. Li et al. (2000) also found that biosolids and compost amendments were highly effective in lowering metal phytoavailability in zinc and cadmium contaminated soil in Palmerton, Pennsylvania. Brown et al. (2003) revegetated contaminated barren soils of the Bunker Hill, Idaho Superfund site by applying a mixture of biosolids and wood ash. This resulted in soils with high phosphate status and reduced the phytoavailability of Zn, Pb, and Cd. It also improved the physical properties of soil. Applications of such biosolids mixtures and or composts appear to offer great promise for revegetation of severely phytotoxic metal contaminated soils (Li et al. 2000).

Table 2-3: Percent (%) Cu in each fraction as influenced by different rates of compost over the incubation study period

Rate of compost	Time period	F1	F2	F3	F4	F5	F6
Control	Day 0	0.54	0.06	16.9	34.9	31.0	16.6
	Day 30	0.40	2.57	11.4	48.5	20.4	16.7
	Day 60	0.30	3.81	16.1	29.0	27.6	23.2
Compost-2.5%	Day 0	0.49	0.06	14.7	21.7	47.6	15.5
	Day 30	0.39	1.15	13.6	44.4	18.8	21.6
	Day 60	0.32	2.79	15.7	24.4	36.9	20.0
Compost-5%	Day 0	0.54	0.09	11.6	7.21	53.6	26.9
	Day 30	0.57	0.94	11.9	40.1	28.6	17.9
	Day 60	0.30	3.25	13.0	20.2	42.2	21.1
Compost-10%	Day 0	0.75	0.18	7.84	6.24	59.0	26.0
	Day 30	0.54	0.59	6.59	33.2	35.1	24.0
	Day 60	0.33	3.29	8.75	22.4	38.5	26.7
Compost-20%	Day 0	0.82	0.15	4.52	1.70	66.8	26.0
	Day 30	0.68	0.37	3.61	20.1	48.6	26.7
	Day 60	0.42	3.52	7.30	8.35	48.4	32.0

### 2.3 Conclusions

At the end of the 60-day incubation study, biosolids and composts increased the nutrient (total N, P, C and plant available P) contents of the stamp sands significantly. The increase was slightly higher in biosolids amended stamp sands compared to composts, except in case of total C. The addition of biosolids and composts also increased the organic matter content of stamp sands, which was most prominent at highest rate of compost amendment followed by the highest rate of biosolids. In both biosolids and compost amendments, Cu was mainly present in bound forms (organic, residual, Al and Fe oxides and carbonate bound fraction). There was no significant increase in Cu

concentrations in the plant-available fraction because of the addition of biosolids and compost. This study showed that stamp sands can be organically fertilized to increase nutrient contents for sustaining vegetation growth without increasing Cu for plant uptake and/or leaching. The findings from this incubation study paved the way for follow-up greenhouse column and panel studies.

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**CHAPTER 3**

**EFFECT OF COMPOST AND PLANT COVER ON THE FATE AND  
DISTRIBUTION OF COPPER AND EROSION CONTROL IN  
CONTAMINATED STAMP SANDS**

**Abstract**

Several million metric tons of stamp sands were generated in the Upper Peninsula of Michigan during extensive copper (Cu) mining activities in the late 19<sup>th</sup> and early 20<sup>th</sup> century. These stamp sands, containing residual Cu, were discharged into various offshoots of Lake Superior. Given the lack of tolerance of Cu toxicity of aquatic organisms, in due course, the sediments were dredged and dumped on the lake shorelines, converting these areas into vast, fallow lands that are not conducive to plant growth. Erosion of these Cu-contaminated stamp sands back to the lakes is severely affecting the benthic community. In this study we grew hardy, cold-tolerant oil seed crops camelina (*Camelina sativa*) and field pennycress (*Thlaspi arvense*) to serve the dual purpose of producing feedstock for biofuels, and providing a vegetative cap, thus reducing the erosion of stamp sands back to the lakes. We made this a complete "green" venture, providing plant nutrients via compost instead of commercially available inorganic fertilizers. The greenhouse column study was undertaken investigating the effects of compost application and plant type, camelina and field pennycress, on the fate and distribution of Cu in the stamp sands collected from Hubbell/Tamarack site in Torch

Lake, MI. The compost was added at rates of 0, 25 (2.5%), 50 (5%), 100 (10%) and 200g (20%) per kg of stamp sand. The experiment was done in triplicates, resulting in a total of 33 columns. The plants germinated and grew in all the columns except in the control. Soil samples and leachates were collected at monthly intervals up to a period of six months. Concentration of Cu ( $\mu\text{g/g}$ ) was highest in roots closely followed by leaves and then pods, seeds and stem in both camelina and field pennycress. The concentration of Cu in all plant parts was more in camelina and field pennycress with compost rate of 2.5 and 5% than 10 and 20%. A follow up field simulation study with two wooden panels was done in the greenhouse at Michigan Tech University. One panel with camelina grown on stamp sands amended with compost (10%) and other panel with stamp sands and no plant cover served as control. The panel with camelina significantly reduced stamp sand erosion in the surface runoff as compared to control. The biofuel quality of camelina was also analyzed by measuring oil content and quality (fatty acid profile).

### **3. Introduction**

Elaborate mining activities from 1860's to 1960's in Upper Peninsula of Michigan have led to copper (Cu) contamination of the environment. Several million metric tons of mine tailings formed during the Cu mining activities in this region. These tailings are called "stamp sands" because they were generated by crushing native Cu containing rocks via a process called stamping. The stamp sands were discharged into Lake Superior, and other interior lakes that are its offshoots. Torch Lake is part of the Keweenaw waterway in the Upper Peninsula of Michigan and connects to Lake Superior

via Portage Lake. The lake was filled with about 200 million tons of stamp sands from the copper industry in over a century from 1868 to 1968 (Cusack and Mihelcic 1999; Weston 2007). The mining companies then dredged the sediments and dumped them on lake shores from early to mid-1900s for copper reclamation activities converting these areas into vast, fallow lands (Weston 2007). In 1983, the Michigan Department of Public Health (MDPH) issued a fish consumption advisory for sauger and walleye due to the high incidence of fish tumors (MDPH 1983; MDNR 1987). In 1986, 14 areas within the Keweenaw Peninsula of Houghton County, Michigan were designated as a Superfund site and they were commonly referred to as the Torch Lake Superfund site (US EPA 1986). US EPA decided to establish a vegetative cap over the stamp sands which surrounded the lake as a part of its remediation work (MDEQ 2007). But, the vegetation has not been able to grow uniformly over the stamp sands and there are numerous bare patches where there is no plant growth at all. Native vegetation could not grow properly because of Cu toxicity, and stamp sands being very low in essential nutrients and water holding capacity.

Now, the Cu contaminated stamp sands are being eroded back into the lakes, thus affecting the aquatic and benthic population again. There are signs installed in June 2015 on Hubbell beach on the Torch Lake shoreline about potential hazards of high concentration of heavy metals in the stamp sands (TLT 2015). It is understood that unless the stamp sands are fertilized to the point of sustaining vegetation growth, the problem with erosion and water quality degradation will continue.

Composts have been historically used as another slow-release, organic source of fertilizer. The establishment of plant cover on stamp sands will reduce the potential of erosion and contaminant transfer into the Torch Lake. During the past decades, worldwide petroleum consumption has increased tremendously due to the growth of human population and industrialization, which has resulted in depletion of fossil fuel reserves and increase in the price of petroleum. The transport sector is heavily dependent on petroleum derived fuels. Therefore, there is a great need for diesel fuel substitution all over the world with a clean, renewable fuel such as biodiesel (Balat and Balat, 2010). Biodiesel is an alternative fuel composed of mono-alkyl esters of long-chain fatty acids and is prepared from vegetable oils or animal fats by a process known as transesterification. Biodiesel has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). Biodiesel possesses significant technical advantages over petrodiesel, such as derivation from renewable feedstocks, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, superior flash point and biodegradability, reduced toxicity, as well as a reduction in exhaust emissions (Mittelbach and Remschmidt, 2004; Knothe et al., 2005; McCormick et al., 2006; Moser, 2009a). Feedstocks for biodiesel production vary considerably with location according to climate and availability. Generally, the most abundant lipid in a particular region is the most common feedstock. Thus, rapeseed oil is predominantly used in Europe, palm oil predominates in tropical countries, and soybean oil and animal fats are primarily used in the United States (Mittelbach and Remschmidt,

2004; Knothe et al., 2005; Moser, 2009a). But, the high cost of commodity vegetable oils, such as soybean oil in the United States, represents a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder, 2007; Retka-Schill, 2008a). Presently, feedstock acquisition accounts for up to 85% of biodiesel production costs (Paulson and Ginder, 2007; Retka-Schill, 2008a). However, many of these oils are quite expensive and also have competing food-related uses. Consequently, the development of alternative feedstock for biodiesel production that meet all or most of the following criteria has attracted considerable research attention: high oil content, low agricultural inputs, favorable fatty acid composition, compatibility with existing farm equipment and infrastructure, production in a sustainable fashion in off-season or in agriculturally undesirable lands, definable growth seasons, and uniform seed maturation rates. Field pennycress (*Thlaspi arvense*) (Moser et al., 2009a) and camelina (*Camelina sativa*) (Moser and Vaughn, 2010) are recent examples of crops which are source of feedstock oils for biodiesel that meet at least a majority of the above criteria.

The greenhouse study to investigate the impact of biofuel feedstock (camelina, field pennycress) on stamp sand erosion in a greenhouse study was done in a greenhouse under controlled environment at Montclair State University, New Jersey. Biosolids had almost the same Cu content as the stamp sands, which made its choice as a fertilizer amendment dubious. So, compost was used to amend stamp sands at four different rates. A follow up to the greenhouse column study was a field simulation study on wooden panels was done in the greenhouse at Michigan Tech University in collaboration with my

committee member (Dr Rupali Datta). Camelina was chosen as the preferred plant as field pennycress took longer time than camelina to flower and produce seeds in the greenhouse at Montclair State University.

The objectives of the greenhouse study column study and subsequent field simulation study were:

1. To study the effect of compost and plant cover (camelina and field pennycress) on the distribution of Cu.
2. To study the effect of compost and plant cover (camelina and field pennycress) on erosion of stamp sands.
3. To evaluate the biofuel quality of the seeds of camelina grown on contaminated stamp sands.

### **3.1 Materials and Methods**

#### ***3.1.1. Soil sampling, preparation and characterization***

Stamp sand was collected from Hubbell/Tamarack site near Torch Lake, Upper Peninsula of Michigan. The physical and chemical properties of stamp sands are listed in table 3-3. Air-dried and sieved (2 mm) soil was used for the determination of pH, electrical conductivity (EC), soil moisture and organic matter content using standard protocols (Sparks 1996). Available P was extracted by Mehlich III solution (Mehlich 1984). Total Cu, Fe, Al and P was determined by acid digestion according to the USEPA Method 3050B (USEPA 1996). The acid digests were analyzed in Inductively Coupled

Plasma – Mass Spectroscopy (ICP-MS). The soil particle size distribution was determined by the pipette method (Gee and Bauder 1986).

### ***3.1.2. Study design and soil amendments***

Compost was bought from a local nursery in Clifton, NJ. Compost was added at rates of 0, 25 g/kg (2.5%), 50 g/kg (5%), 100 g/kg (10%) and 200 g/kg (20% stamp sand). A total of 33 columns were used for the greenhouse study (Table 3-1). 3.50 kg of stamp sand was used in each column. The total amount of compost used was 7.88 kg (oven dry weight). The stamp sand was sieved through a 2.0 mm sieve. The lower 6 inches of the columns was filled with uncontaminated play sand. The stamp sand was mixed thoroughly with different rates of compost according to the experimental design. The soil amendments were poured uniformly on the top of play sand in the different columns. The soil amendments were equilibrated for 10 days by adding water according to their water holding capacities. After 10 days of equilibration, 20 seeds of camelina/field pennycress were sown in one column according to the experimental design. The plants were irrigated according to their water requirement and water holding capacities of the soil amendments. Each column was connected to a 1 L bottle to collect leachate. The leachates were collected at a monthly interval and analyzed for Cu and P in ICP-MS. The seeds were harvested from camelina and field pennycress at maturity and weighed for all the different rates of compost.



Table 3-1: Design of the greenhouse column experiment

Treatments	Plant type	Replications	No. of columns
Stamp sand only	No plant	3	3
Stamp sand only	Camelina	3	3
Stamp sand only	Field pennycress	3	3
Stamp sand-compost (2.5%)	Camelina	3	3
Stamp sand-compost (5%)	Camelina	3	3
Stamp sand-compost (10%)	Camelina	3	3
Stamp sand-compost (20%)	Camelina	3	3
Stamp sand-compost (2.5%)	Field pennycress	3	3
Stamp sand-compost (5%)	Field pennycress	3	3
Stamp sand-compost (10%)	Field pennycress	3	3
Stamp sand-compost (20%)	Field pennycress	3	3

The columns were cylindrical in shape and each column measured 40 cm in length and 15 cm in diameter. The columns were allowed to equilibrate keeping the soils moist by applying water according to 75% of water holding capacity of respective soils for a time period that would have been optimized by the laboratory studies. The temperature of the greenhouse was set at about 25 C during the experiment. The columns were watered according to the water requirement of the plants and water holding capacities of respective soils. The soil samples were taken at regular intervals (every 30 days) and analyzed for Cu and in ICP-MS. The leachates were also analyzed periodically (every 30 days) for dissolved Cu, P, turbidity and total suspended solids (TSS). This indicated the mobility of Cu and P in a column as influenced by plant cover and organic matter. These leachates were compared with the leachates from the columns with no plants for soil particles so as to evaluate the efficiency of the plants in reducing soil

erosion. This was to observe if soil particulates in the leachates could act as a proxy for erosion.

The crops were harvested at maturity (after the formation of seeds). The plant, soil and leachate samples were also taken before harvesting of the plants. The plant samples (excluding seeds) were washed and dried in the hot air oven at 65 °C for 3 days and plant parts were separated into roots, stem, leaves, pods and seeds and dry matter yields of these plant parts were recorded. The oven dried plant, soil and leachates were acid digested by following the USEPA Method 3050B (USEPA 1996). The samples were diluted, filtered and then analyzed for Cu in ICP-MS.

### ***3.1.3. Study design and soil amendments – Panel study***

A field simulation study was done in the greenhouse at Michigan Tech University in July, 2015 after the column study at Montclair State University. The compost which was used in greenhouse column study was purchased from the same local nursery in NJ and shipped to Michigan Tech University. The compost was air dried and subsequently further moisture in the compost was determined by drying of 3 g of compost (n=3) in a hot air oven at 105 °C for 24 hours. The air dried compost was added at a rate of 100 g/kg (10% of stamp sand) to the two wooden panels measuring 4ft (length) x 3ft (width) x 1 ft (depth) (Table 3-2). The panels had an internal slope of 10 degrees. It was connected to a partially open PVC pipe at the top front end of the panel that acted as a conduit for the surface runoff. The PVC pipe was then connected to an 8 gallon tote at its other end via

another pipe going into the tote. There were pipes at three locations at the bottom of the panel to act as conduits for the collection of leachate in an 8 gallon tote placed on the ground.

The stamp sand and compost were sieved through a 2.0 mm sieve. The lower 5 inches of a panel was filled with 10 bags (22.7 kg each) of uncontaminated play sand which was purchased from Lowes (hardware store) in Marquette, MI. The stamp sand was mixed thoroughly with compost. The soil amendment was poured uniformly on the top of play sand in the panels. The soil amendments were equilibrated for 10 days by adding water according to their water holding capacity. After 10 days of equilibration, seeds of camelina were sown in one panel and the other panel was left bare to act as a control.

The plants were irrigated according to their water requirement and water holding capacity of the soil amendment. The surface runoff and leachates were collected by simulating a rainfall event every two months. The panel was showered with water by keeping two shower heads over the panel ensuring uniform distribution simulating rainfall. The time duration of each rainfall simulation event, pressure and discharge of water was kept constant for all the three rainfall simulation events. The seeds were harvested from camelina at maturity and weighed. The temperature of the greenhouse was set at about 25 °C during the experiment. The surface runoff and leachates were also analyzed for dissolved Cu, P, turbidity and TSS. This will indicate the mobility of Cu and

P in a column as influenced by dissolved organic matter. The presence or absence of soil particles (stamp sands) in surface runoff helped in determining the efficiency of camelina in controlling stamp sand erosion.

The crops were harvested at maturity after the formation of seeds. The soil, runoff and leachate samples were also taken before harvesting of the plants. The roots, shoots and seeds of the plants were collected. The plant samples were washed and dried in the oven at 65 °C for 3 days. The plant parts (roots, stem, leaves, pods and seeds) were separated and dry matter yield of each was recorded separately. The oven dried plant samples (roots, stem, leaves, pods and seeds), soil samples, surface runoff and leachates were analyzed for Cu in ICP-MS by following the standard methods.

Table 3-2: Design of the field simulation panel experiment

Soil type	Treatment	No. of replications	No. of panels
Stamp sand	Camelina – Stamp sand – Compost	1	1
	Stamp sand-Compost-no plant (control)	1	1

#### ***3.1.4. Oil content and quality analysis***

The oil, protein and moisture content of camelina seeds was analyzed by Nuclear Magnetic Resonance Spectrometry (NMR), a non-destructive technology, by the seed laboratory (International Seed Testing Association (ISTA) accredited) of Oregon State University, Corvallis, Oregon. The same seed samples of camelina were used for

analyzing the complete fatty acid profile of camelina seeds by SGS North America Inc., Agricultural Services, St. Rose, Louisiana.

### ***3.1.5. Organic matter, carbon and nitrogen analysis***

The organic matter content was measured in the samples by loss on ignition method (Schulte and Hopkins 1996). The samples were weighed (3 g) in crucibles and kept in a hot air oven at 105 °C for 24 hours. After oven drying the samples, the samples were weighed again to account for soil moisture, then kept in the muffle furnace and maintained at 360 °C for 2 hours. The samples were cooled and weighed to observe the loss in weight which accounted for soil organic matter (Schulte and Hopkins 1996). Total C and total N were measured in samples using a Perkin-Elmer 2400 CHN analyzer (Nelson and Sommers 1982). 10-20 mg of oven dried soil samples were weighed and wrapped in aluminum foil and analyzed for total C and total N in the CHNS analyzer (Nelson and Sommers 1982).

### ***3.1.6. Statistical analysis***

The data were statistically analyzed using the statistical software JMP version 10 (SAS 2012). Means were compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ) to test for significant difference among different levels of compost and plant cover.

## 3.2 Results and discussion

### 3.2.1. Properties of soil and amendments

The properties of the stamp sands and compost are given in table 3-3. The stamp sands were slightly alkaline (8.2) in nature. Compost had a near neutral pH (6.9). The stamp sand had an electrical conductivity (EC) of 83  $\mu\text{S}/\text{cm}$ , which was expected given its very sandy texture, and very low water/salt holding capacity, whereas compost had EC of 1840  $\mu\text{S}/\text{cm}$ . Stamp sands had an organic matter content of 0.5% whereas compost had organic matter contents of 84%, respectively.

Table 3-3: Physicochemical properties of soil and compost

Properties	Stamp sand	Compost
pH	8.2	6.9
EC <sup>a</sup> ( $\mu\text{S}/\text{cm}$ )	83	1840
SOM <sup>b</sup> (%)	0.5	84
Sand (%)	95	-
Silt (%)	2.5	-
Clay (%)	2.5	-
Cu (mg/kg)	719	54
Fe (mg/kg)	6200	-
Al (mg/kg)	2300	-
Plant Available P (mg/kg)	0.70	1009
Total P (mg/kg)	800	2090
Total N (g/kg)	1.81	388

<sup>a</sup> EC = electrical conductivity

<sup>b</sup> SOM = soil organic matter

The stamp sands, as the name implies, were sandy in texture with 95% sand, and 2.5% each of silt and clay. The Cu concentration in stamp sands and compost was 719

and 54 mg/kg, respectively. The concentrations of total iron (Fe) and aluminum (Al) in stamp sands were 6200 and 2300 mg/kg, respectively. Stamp sands had a total and plant available phosphorus (P) content of 800 and 0.7 mg/kg, respectively. Compost had a total and plant available P as 2090 and 1009 mg/kg, respectively. The nitrogen (N) content in stamp sands, biosolids and compost was 1.81 and 388 g/kg, respectively. The remediation work done by US EPA on the Torch Lake superfund site in 2005 (MDEQ 2007) may have increased the total P content of stamp sands. But, as evidenced from the Mehlich 3 results (Table 3-2), a very small fraction of that total P is plant available (less than 0.1%); rest of the P in stamp sands is in bound forms, and not available to plants.

### ***3.2.2. Cu distribution in plants (camelina and field pennycress)***

Cu concentration ( $\mu\text{g/g}$ ) in roots of camelina and field pennycress (Fig. 3-1) was significantly higher in low rates of compost (2.5 and 5%) as compared to high rates of compost (10 and 20%). In case of camelina, Cu concentration in roots was more than that of field pennycress at all rates of compost and significantly higher at compost rate of 2.5%. Cu concentrations ( $\mu\text{g/g}$ ) in stems of camelina (Fig. 3-2) were significantly higher in low rates of compost (2.5% and 5%) than high rates of compost (10% and 20%). In case of field pennycress, Cu concentrations in stems (Fig. 3-2) were almost same at compost rates of 2.5%, 5% and 10% but were significantly higher than in maximum compost rate (20%). In stems of camelina, Cu concentration was significantly higher than in stems of field pennycress at all rates of compost.

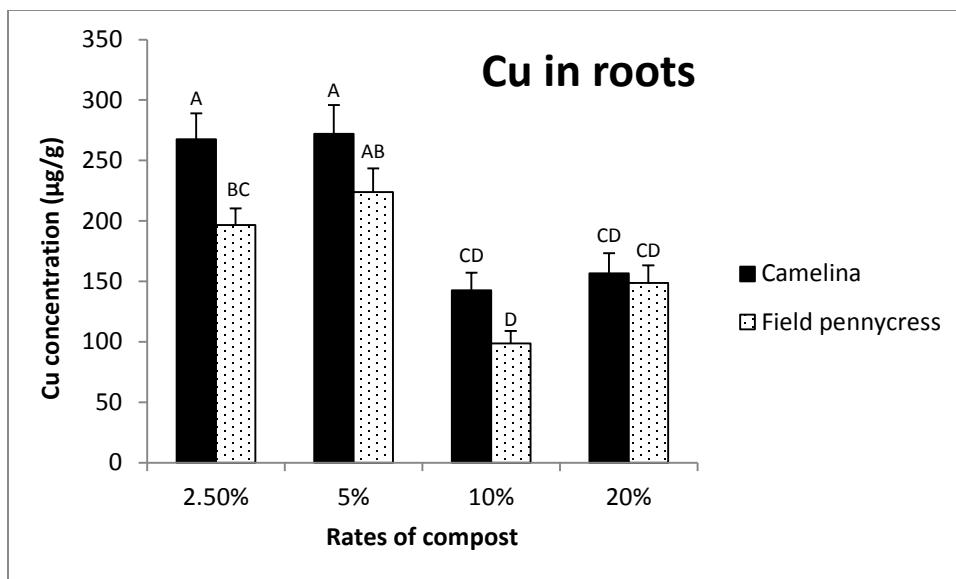


Fig. 3-1: Total Cu (mg/kg) in roots of camelina and field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

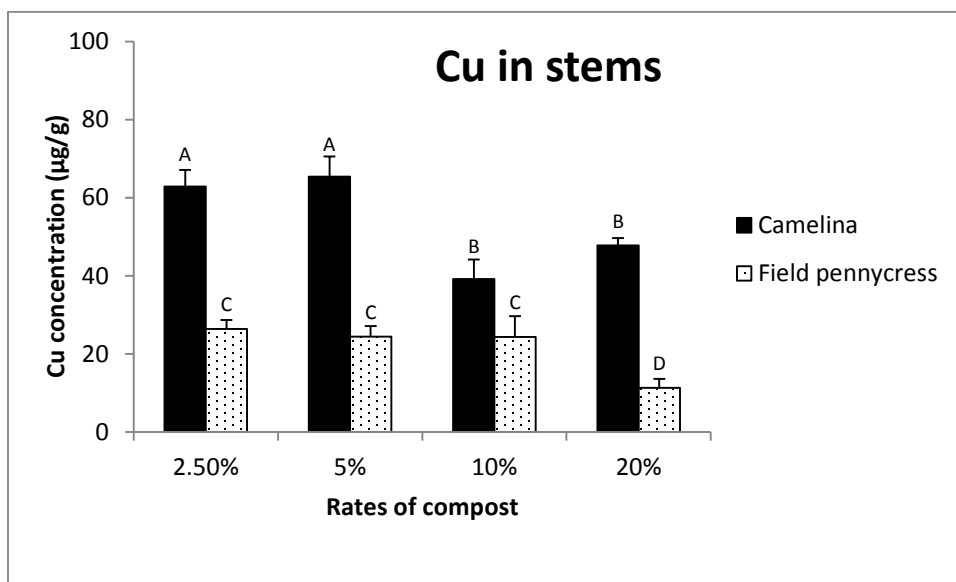


Fig. 3-2: Total Cu (mg/kg) in stems of camelina and field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.



Cu concentrations ( $\mu\text{g/g}$ ) in leaves of camelina (Fig. 3-3) were higher in low rates of compost (2.5% and 5%) than high rates of compost (10% and 20%). Cu concentration in leaves of camelina at maximum compost rate was significantly less than in camelina leaves at other rates of compost (2.5%, 5% and 10%). In case of field pennycress, Cu concentrations in leaves (Fig. 3-3) at low compost rates (2.5% and 5%) were significantly more than in leaves at high compost rates (10% and 20%). In leaves of camelina, Cu concentration was significantly higher than in leaves of field pennycress at all rates of compost.

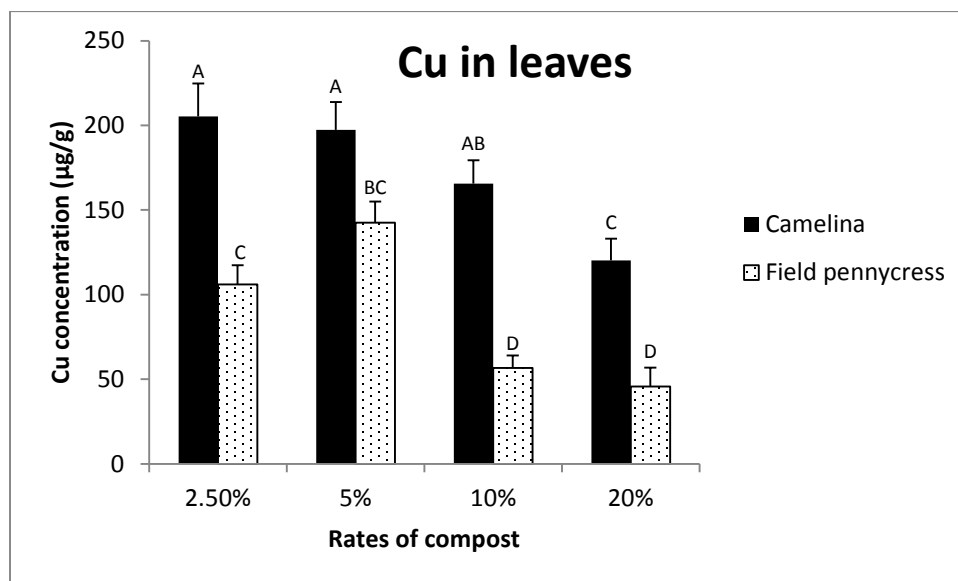


Fig. 3-3: Total Cu (mg/kg) in leaves of camelina and field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different

Cu concentrations ( $\mu\text{g/g}$ ) in pods of camelina (Fig. 3-4) were significantly higher in low rates of compost (2.5% and 5%) than high rates of compost (10% and 20%). In case of field pennycress, Cu concentrations in pods (Fig. 3-4) were almost same at compost rates of 2.5%, 5% and 20% but Cu concentration was higher in compost rate of 10%. In pods of camelina, Cu concentration was significantly higher than in pods of field pennycress at low rates of compost (2.5%, 5%).

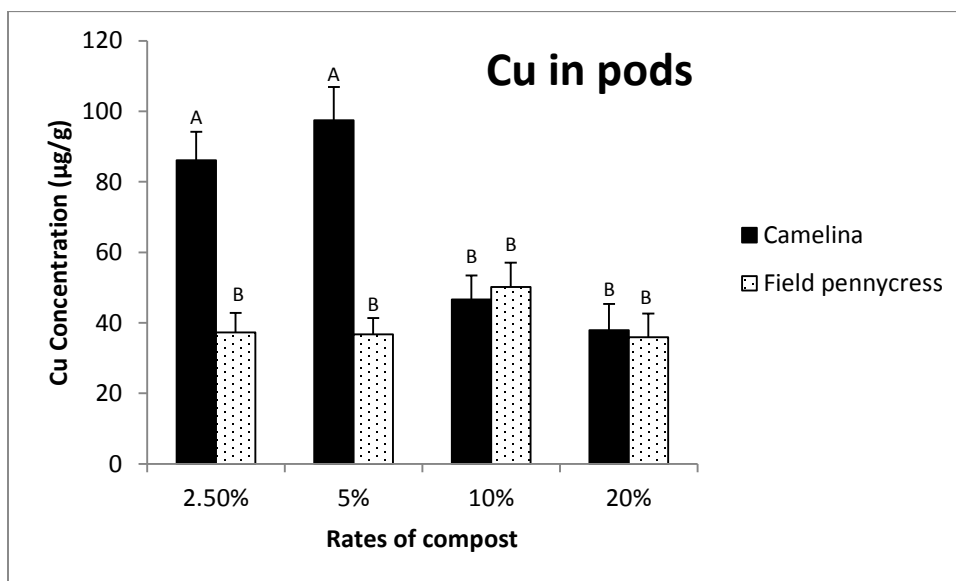


Fig. 3-4: Total Cu ( $\text{mg/kg}$ ) in pods of camelina and field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Cu concentrations ( $\mu\text{g/g}$ ) in seeds of camelina (Fig. 3-5) were significantly higher in low rates of compost (2.5% and 5%) than high rates of compost (10% and 20%). Cu concentration in seeds of camelina at lowest rate of compost was significantly more than

at other compost rates. In case of field pennycress, Cu concentrations in seeds (Fig. 3-5) were almost same at compost rates of 5%, 10% and 20% but Cu concentration was higher in compost rate of 2.5%. In seeds of camelina, Cu concentration was significantly higher than in seeds of field pennycress at all rates of compost except 10%.

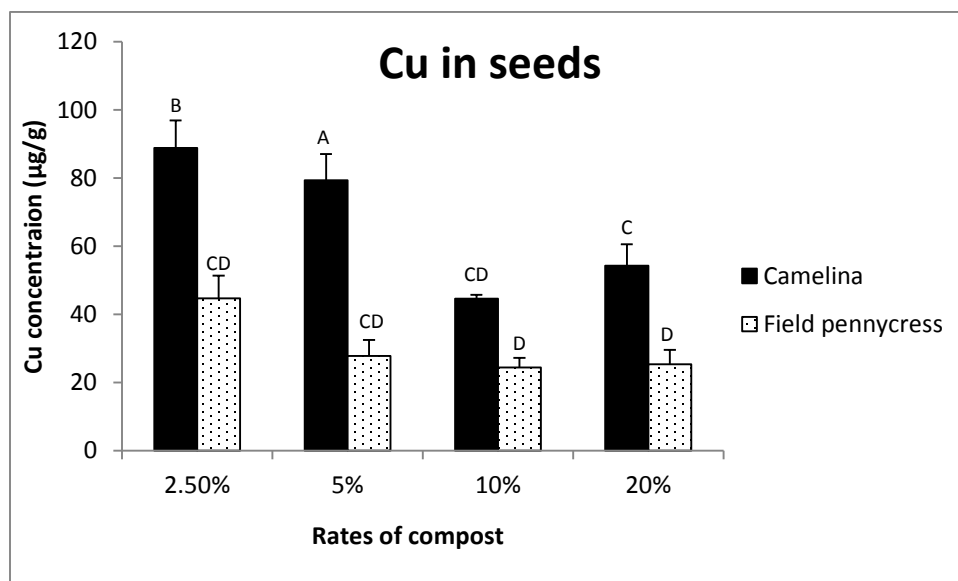


Fig. 3-5: Total Cu (mg/kg) in seeds of camelina and field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Cu concentration of Cu ( $\mu\text{g/g}$ ) was highest in roots (Fig. 3-1) closely followed by leaves (Fig. 3-2) and then pods (Fig. 3-4), seeds (Fig. 3-5) and stem (Fig. 3-2) in camelina and field pennycress.

### ***3.2.3. Cu distribution in leachates***

In columns with camelina, dissolved Cu concentration (mg/L) was maximum and significantly higher in the leachates from columns with compost rate of 20% followed by 10, 5, 2.5% compost, and control (Fig. 3-6). Concentration of Cu in the leachates from columns of camelina in the first two months was quite small but increased subsequently and became highest in the third month and decreased thereafter. The highest Cu concentration in camelina was 115 mg/L in leachate of column with compost rate of 20% in the third month (Fig. 3-6).

In field pennycress columns, dissolved Cu concentration (mg/L) followed the same trend as in case of camelina, it was maximum and significantly higher in the leachates from columns with compost rate of 20% followed by 10, 5, 2.5% compost, and control (Fig. 3-7). Also, Cu concentration in leachates from columns of field pennycress in the first two months was quite small but increased subsequently and became highest in the third month and decreased thereafter. The highest Cu concentration in field pennycress was 66 mg/L in leachate of column with compost rate of 20% in the third month (Fig. 3-7).

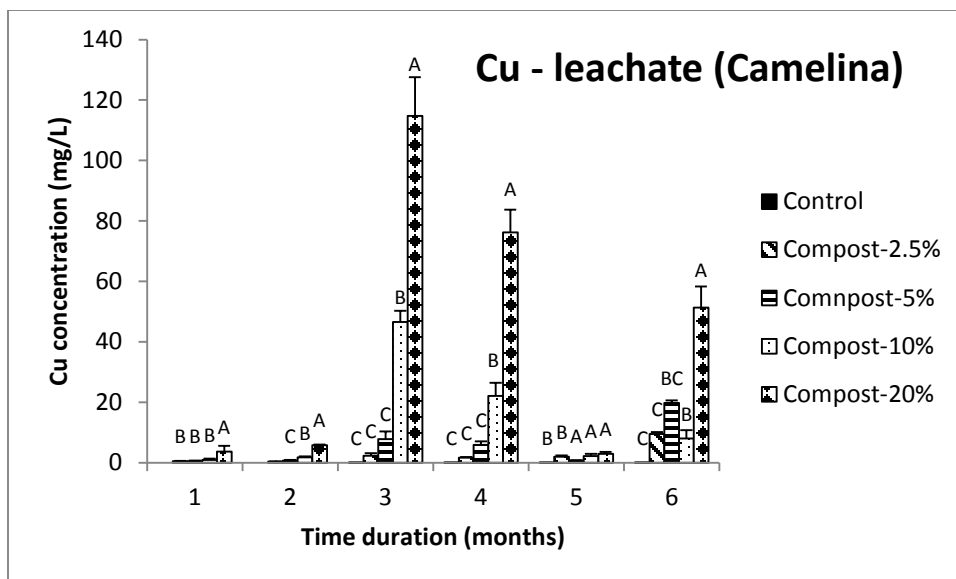


Fig. 3-6: Cu (mg/L) in leachates of camelina as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

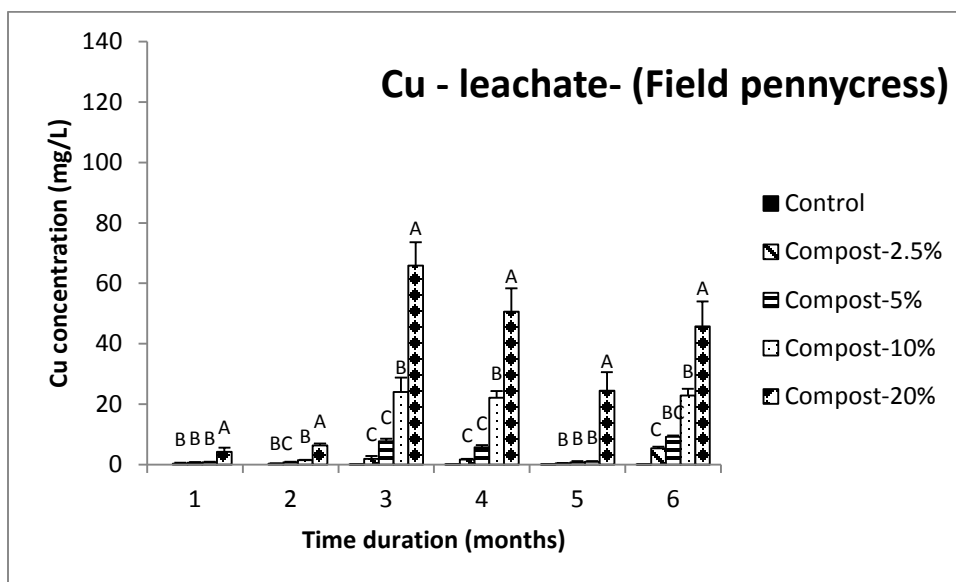


Fig. 3-7: Cu (mg/L) in leachates of field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.4. Cu distribution in soil

There was not a significant change in the Cu concentration (mg/kg) in soil in all the columns (control, camelina and field pennycress; Figs. 3-8, 3-9) during the study period.

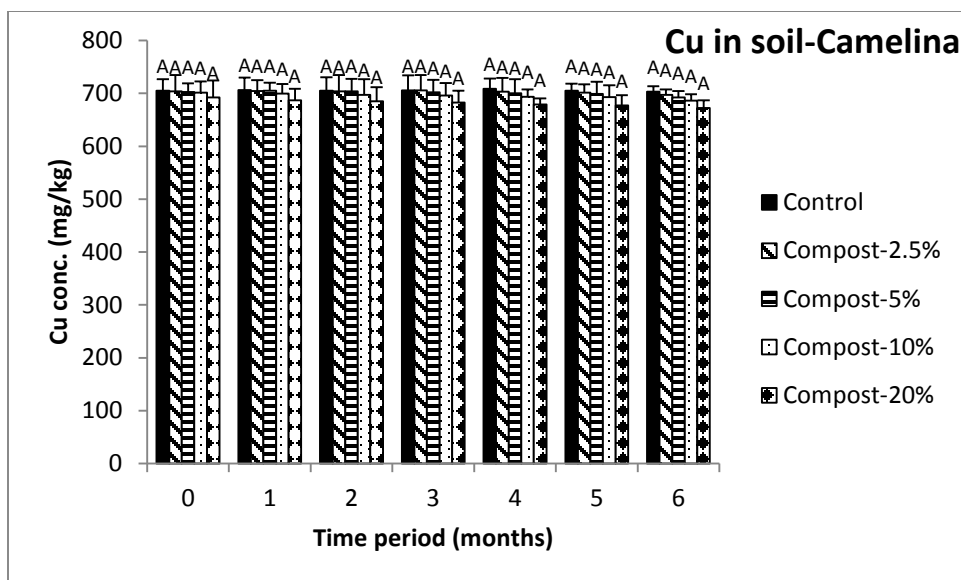


Fig 3-8: Total Cu (mg/kg) in soil in camelina during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

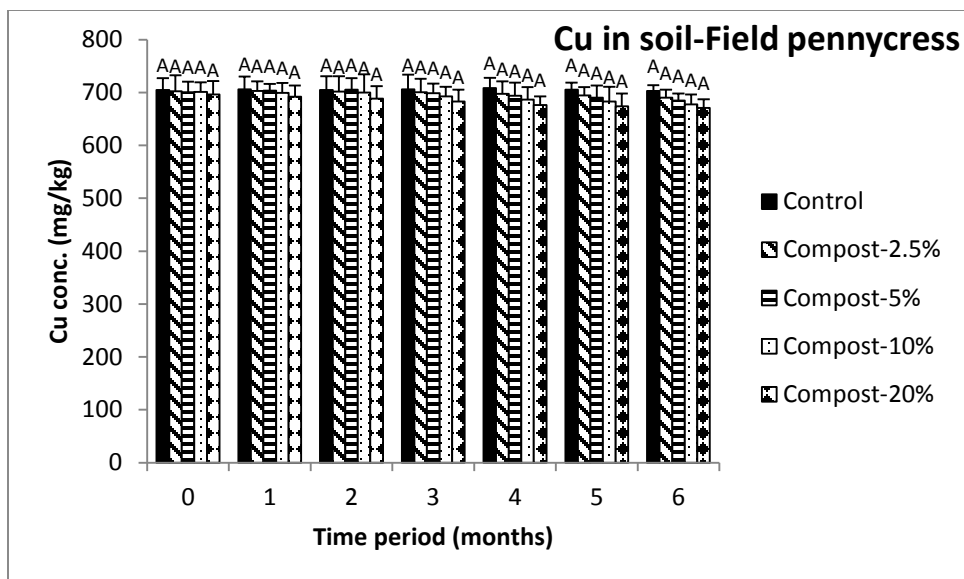


Fig 3-9: Total Cu (mg/kg) in soil in camelina during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different

### 3.2.5. P distribution in leachates

In columns with camelina, dissolved P concentration (mg/L) was maximum and significantly higher in the leachates from columns with compost rate of 20% followed by 10, 5, 2.5% compost, and control (Fig. 3-10). Concentration of P in the leachates from columns of camelina in the first two months was quite small but increased subsequently and became highest in the third month and decreased thereafter. The highest P concentration in field pennycress column was 2350 mg/L in leachate of third month (Fig.3-10).

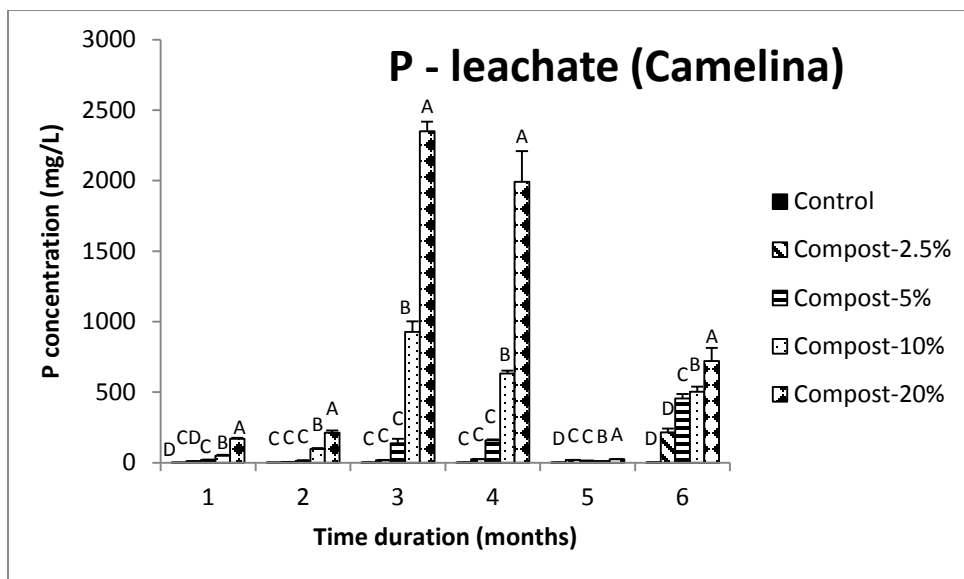


Fig.3-10: P (mg/L) in leachates of camelina as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

In columns with field pennycress, dissolved P concentration (mg/L) was maximum and significantly higher in the leachates from columns with compost rate of 20% followed by 10, 5, 2.5% compost, and control (Fig. 3-11). Concentration of P in the leachates from columns of field pennycress in the first two months was quite small but increased subsequently and became highest in the third month and decreased thereafter. The highest Cu concentration in field pennycress column was 66 mg/L in leachate of third month (Fig.3-11).



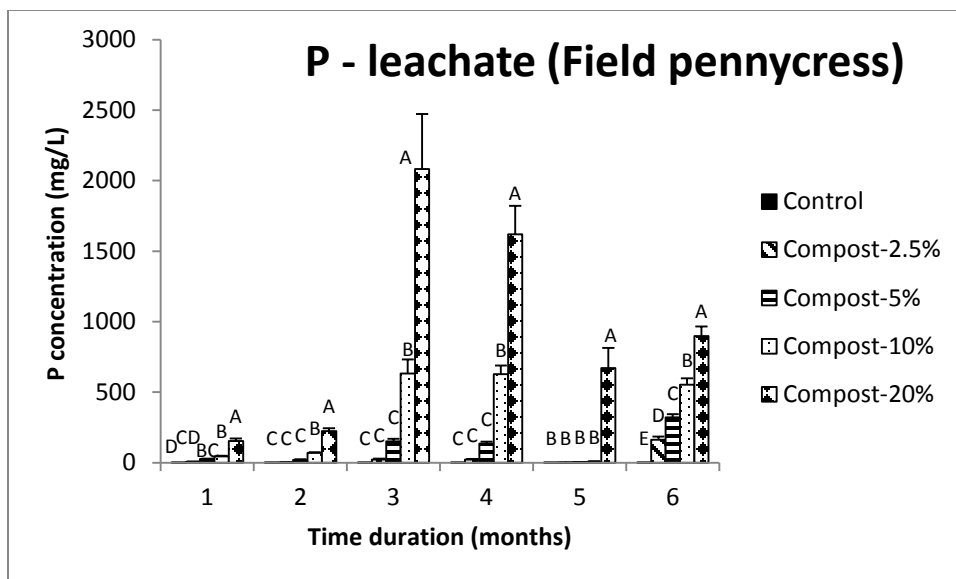


Fig. 3-11: P (mg/L) in leachates of field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.6. Turbidity in leachates

The turbidity (NTU) in the leachates of camelina (Fig. 3-12) and field pennycress (Fig. 3-13) columns measured periodically (every month) during the study period did not display any specific trend. The measurement of turbidity in the leachates of the columns could not act as a proxy for the measurement of stamp sand erosion. Therefore, we decided to measure turbidity and total suspended solids (TSS) in the surface runoff of the panels as an indicator of stamp sand erosion in the field simulation study.

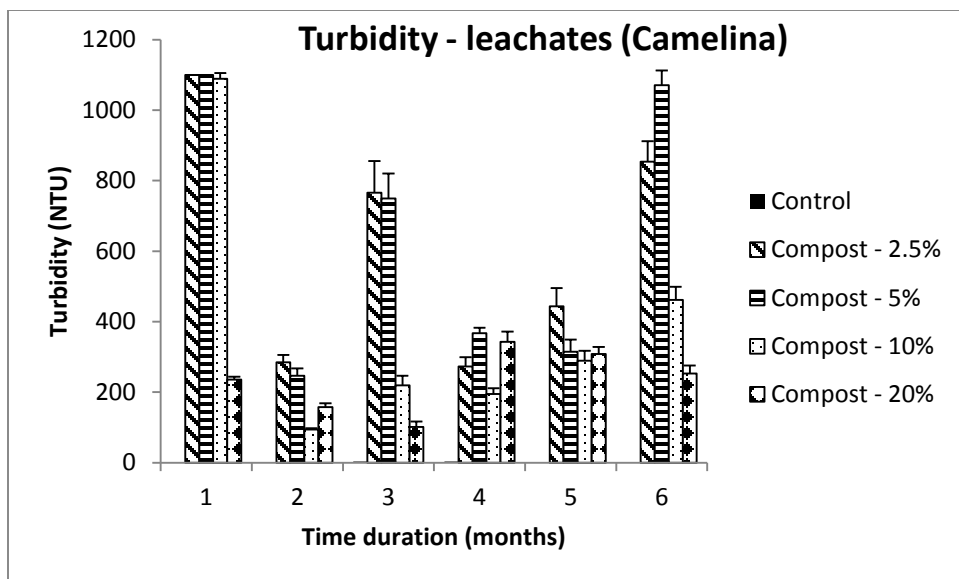


Fig. 3-12: Turbidity (NTU) in leachates of field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D.

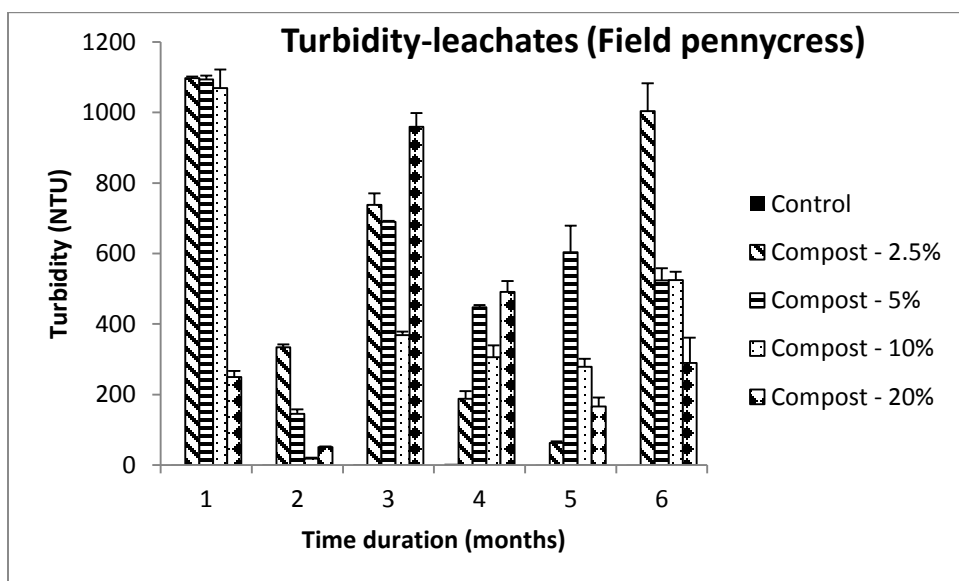


Fig. 3-13: Turbidity (NTU) in leachates of field pennycress as affected by different rates of compost during the study period. Data is reported as mean  $\pm$  S.D.

### ***3.2.7. Plant biomass of camelina and field pennycress***

In case of camelina, the oven dry weight of roots increased with increase in compost rate except compost 10% but the increase was not statistically significant across different compost rates (Table 3-4). The oven dry weight of stem increased with increasing compost rates and the increase was significant at compost rate of 10% and 20%. The oven dry weight of leaves increased with increasing compost rates and the increase was significant at the maximum compost rate of 20%. The oven dry weight of pods did not show any specific trend with increasing compost rates with maximum and significant weight in camelina plants at compost rate of 10%. In case of camelina seeds, the oven dry weight followed the same trend as in camelina pods with maximum seed weight in columns with compost rate of 10%. The total plant biomass of camelina increased with increasing compost rates with significant yield increases in columns with compost rates of 10 and 20%.

In case of field pennycress, the oven dry weight of roots increased with increase in compost rate and the increase was statistically significant in plants in columns with compost rates of 10 and 20%. (Table 3-4). The oven dry weight of stem increased with increasing compost rates and the increase was significant in field pennycress plants in columns with the maximum compost rate of 20%. The oven dry weight of leaves increased with increasing compost rates and the increase was significant in plants grown in columns in the compost rate of 10 and 20%. The oven dry weight of pods increased in

field pennycress plants with increasing compost rates and significant increase was recorded in plants at compost rate of 20%.

Table 3-4: Plant yield (oven dried; g) of camelina and field pennycress in the column study

Camelina	Roots	Stem	Leaves	Pods	Seeds	Total biomass
Compost-2.5%	0.08 <sup>c</sup>	0.96 <sup>c</sup>	0.47 <sup>c</sup>	0.12 <sup>d</sup>	0.09 <sup>c</sup>	1.72 <sup>e</sup>
Compost-5%	0.14 <sup>c</sup>	0.97 <sup>c</sup>	0.58 <sup>c</sup>	0.05 <sup>d</sup>	0.04 <sup>bc</sup>	1.78 <sup>e</sup>
Compost-10%	0.12 <sup>c</sup>	2.10 <sup>b</sup>	0.85 <sup>c</sup>	0.51 <sup>b</sup>	0.37 <sup>bc</sup>	3.96 <sup>cd</sup>
Compost-20%	0.44 <sup>bc</sup>	3.53 <sup>a</sup>	2.86 <sup>b</sup>	0.18 <sup>cd</sup>	0.19 <sup>bc</sup>	7.21 <sup>b</sup>
Field pennycress						
Compost-2.5%	0.11 <sup>c</sup>	0.50 <sup>c</sup>	0.68 <sup>c</sup>	0.24 <sup>cd</sup>	0.21 <sup>bc</sup>	1.74 <sup>e</sup>
Compost-5%	0.11 <sup>c</sup>	0.81 <sup>c</sup>	1.31 <sup>c</sup>	0.35 <sup>bc</sup>	0.30 <sup>bc</sup>	2.89 <sup>de</sup>
Compost-10%	0.78 <sup>ab</sup>	0.81 <sup>c</sup>	2.76 <sup>b</sup>	0.53 <sup>b</sup>	0.65 <sup>b</sup>	5.53 <sup>c</sup>
Compost-20%	1.03 <sup>ab</sup>	2.26 <sup>b</sup>	8.05 <sup>a</sup>	1.40 <sup>a</sup>	1.30 <sup>a</sup>	14.0 <sup>a</sup>

Data is reported as mean (n=3). Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

In case of field pennycress seeds, the oven dry weight followed the same trend as in field pennycress pods with maximum seed weight in columns with compost rate of 20%. The total plant biomass of field pennycress increased with increasing compost rates with significant yield increases in columns with compost rates of 10 and 20%.

### 3.2.8. Mass balance of Cu in greenhouse column study

In case of camelina, the uptake of Cu ( $\mu\text{g}$ ) in stems and leaves increased with increase in compost rate. Cu uptake followed the same trend in roots except at compost rate of 10%. There was no specific trend of Cu uptake in pods and seeds of camelina as

affected by compost rate. But, the total plant uptake of Cu in camelina increased with increasing compost rate. In case of field pennycress, the uptake of Cu ( $\mu\text{g}$ ) in roots, stems and leaves increased with increase in compost rate except in stem and leaves, it decreased at compost rate of 10%. There was also no specific trend of Cu uptake in pods of field pennycress as affected by compost rate as well. The uptake of Cu in seeds decreased at compost rate of 5% and then increased with compost rate. But, the total plant uptake of Cu in field pennycress increased with increasing compost rate.

In both camelina and field pennycress, Cu uptake was highest in leaves, followed by stem, roots, pods, and seeds in owing to high biomass of leaves and stem. In camelina and field pennycress, total plant uptake of Cu in all compost rates combined was 1.30 and 1.31 mg, respectively. In case of leachates, Cu content (mg) in leachates increased with increasing compost rate. In camelina and field pennycress, amount of Cu in leachates in all compost rates combined was 203 and 165 mg, respectively. The majority of Cu was still held in the stamp sands although small amounts of Cu went into the leachate.

Table 3-5: Mass balance of Cu for the greenhouse column study

	Roots (mg)	Stem (mg)	Leaves (mg)	Pods (mg)	Seeds (mg)	Total plant uptake (mg)	Total Cu (leach ates; mg)	Total Cu (Soil; mg)
Control (No plant)	-	-	-	-	-	-	0.05	1757
Camelina								
Compost-2.5%	0.02	0.06	0.01	0.01	0.01	0.11	8.69	1733
Compost-5%	0.04	0.06	0.12	0.01	0.003	0.23	20.0	1709
Compost-10%	0.02	0.08	0.14	0.02	0.02	0.28	43.3	1671
Compost-20%	0.07	0.17	0.34	0.01	0.01	0.60	131	1550
Field pennycress								
Compost-2.5%	0.02	0.01	0.07	0.04	0.01	0.15	5.78	1719
Compost-5%	0.03	0.02	0.19	0.04	0.01	0.29	14.4	1697
Compost-10%	0.08	0.02	0.16	0.05	0.02	0.33	37.4	1654
Compost-20%	0.15	0.03	0.37	0.04	0.03	0.62	106	1570

### ***3.2.9. Field simulation study (greenhouse panel study); Total Suspended Solids (TSS) and Turbidity in surface runoff***

Total suspended solids (TSS; g/L) were significantly higher (5, more than 7 and almost 8 times) in the three surface runoff samples collected at a 2 month interval in the control panel with no plants as compared to the panel with camelina (Fig. 3-14).

Turbidity in the surface runoff samples also followed the same trend as in case of TSS with turbidity values at least 4 times higher in control than camelina panel (Fig. 3-15).

This indicates the effectiveness of a sustained plant cover in reducing stamp sand erosion.

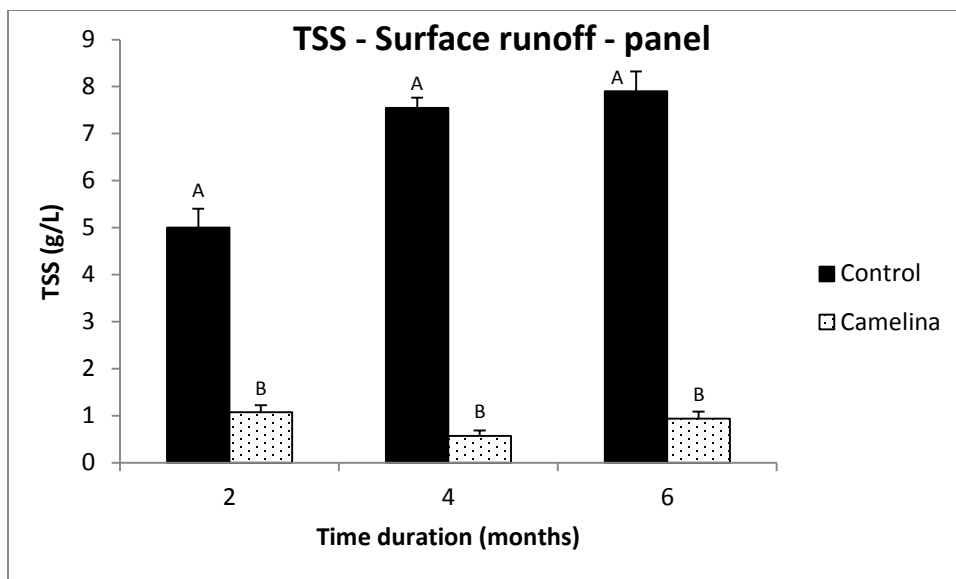


Fig. 3-14: Total Suspended Solids (TSS) in surface runoff in control and camelina panels. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

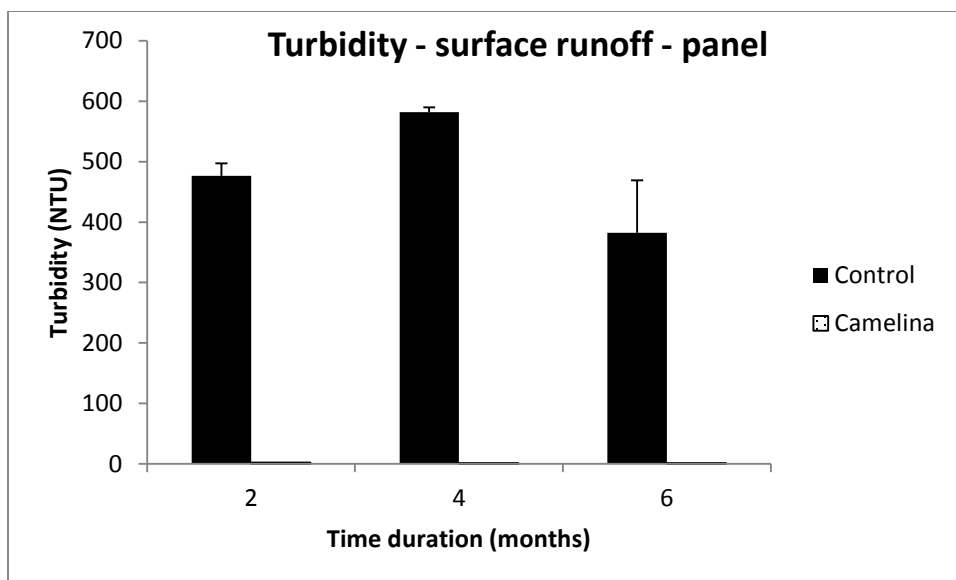


Fig. 3-15: Turbidity (NTU) in the surface runoff in the control and camelina panels. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.10. Cu in surface runoff

The dissolved Cu concentration (mg/L) in surface runoff in control panel was significantly higher than in the panel with camelina plants (Fig. 3-16). In samples taken after 4 and 6 months after sowing of camelina, Cu concentration in the surface runoff was more than four times higher than in the camelina panel. This could be due to the presence of stamp sand particles due to stamp sand erosion in surface runoff of control panel can lead to high dissolved Cu concentration in that water.

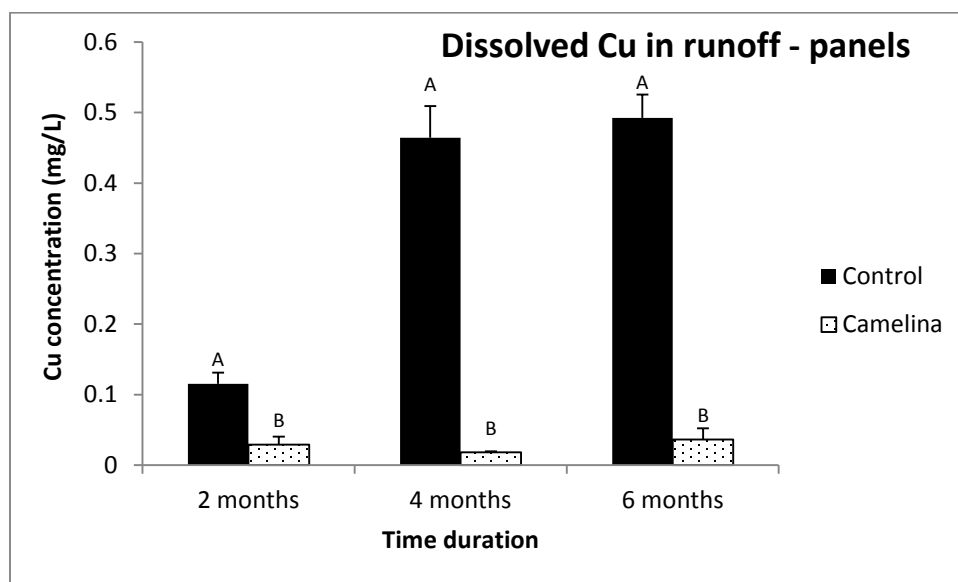


Fig. 3-16: Dissolved Cu (mg/L) in runoff in control (no plant) and camelina panels during the study period. Data is reported as mean ( $n=3$ )  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Total Cu concentration (mg/L) in surface runoff in control panel was significantly higher than in the panel with camelina plants (Fig. 3-17). In samples taken after 4 months



after sowing of camelina, Cu concentration in the surface runoff was more than 25 times higher than in the camelina panel. The high concentration of total Cu in surface runoff as compared to dissolved Cu can be explained by the presence of stamp sand particles due to stamp sand erosion in surface runoff of control panel.

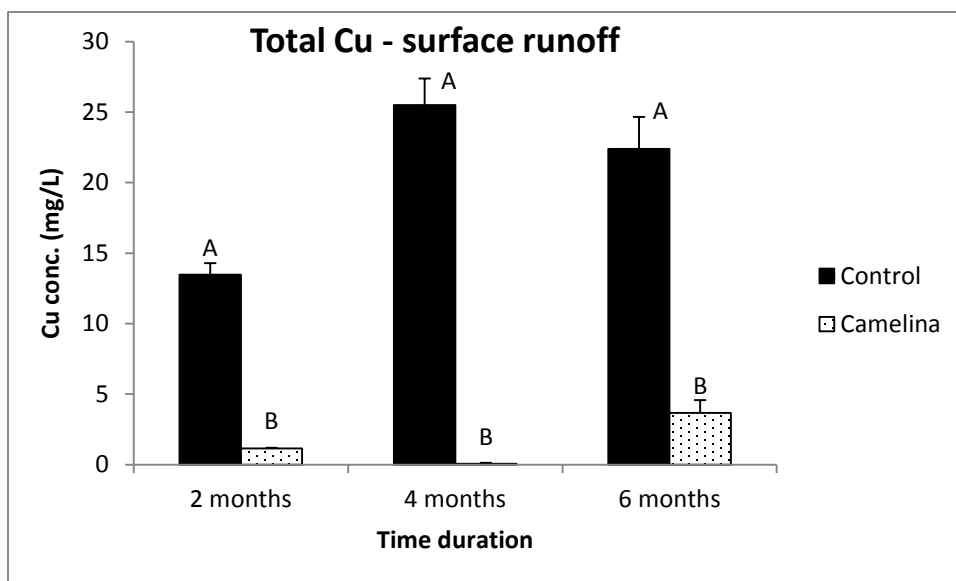


Fig. 3-17: Total Cu (mg/L) in runoff in control (no plant) and camelina panels during the study period. Data is reported as mean ( $n=3$ )  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.11. Cu in leachates

The dissolved Cu concentration (mg/L) in leachates in the control panel was almost same as in camelina panel after two months of camelina sowing (Fig. 3-18). But, in the leachate samples taken after 4 and 6 months, the Cu concentration in the control panel was significantly lower than camelina panel.

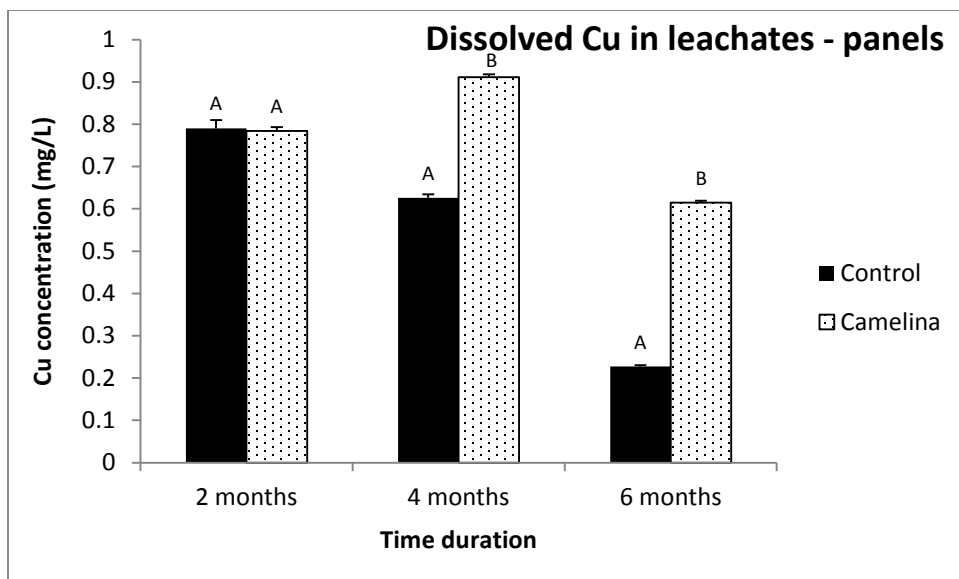


Fig. 3-18: Dissolved Cu (mg/L) in leachates in control (no plant) and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

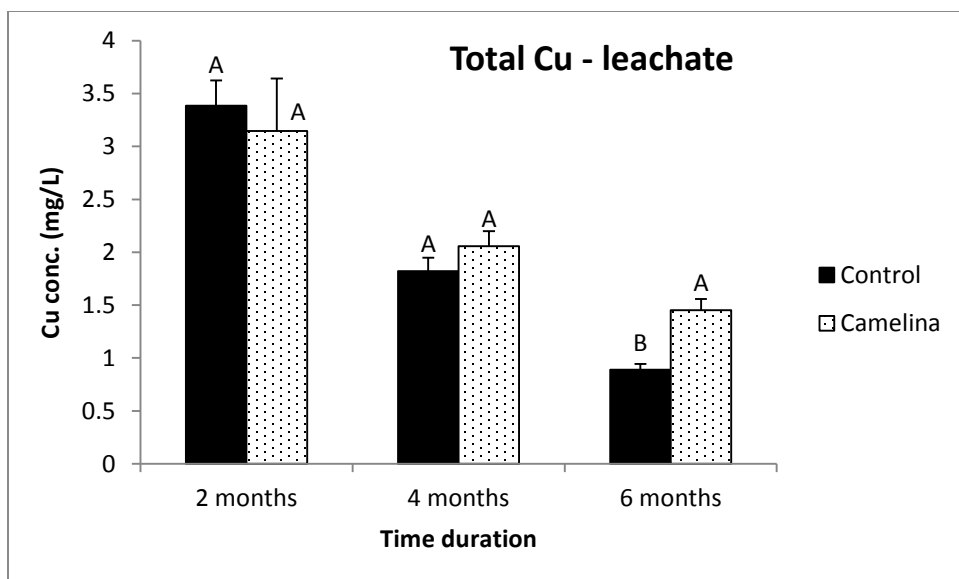


Fig. 3-19: Total Cu (mg/L) in leachates in control (no plant) and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Total Cu concentration (mg/L) in leachates in the control panel was not significantly different from the camelina panel after 2 and 4 months of camelina sowing (Fig. 3-19). But, in the leachate samples taken after 6 months, the Cu concentration in the control panel was significantly lower than camelina panel.

Soil erosion, leaching (Yingming and Corey, 1993) and deep ploughing (Flores Velez et al., 1996) are the three main processes that lead to the redistribution of Cu in the soil. With increase in soil organic matter, the bioavailability of Cu has been reported to decrease (Delas, 1984; Gupta and Aten, 1993) as Cu forms stable complexes with dissolved organic matter (DOC) in solution and increased DOC levels reduce free ionic  $\text{Cu}^{2+}$  activity (Stevenson, 1994; RoÈmkens, 1998). Plants also influence chemical conditions in the soil as root growth increases soil organic matter especially around rhizosphere which in turn stimulates bacterial growth (Schulin et al., 1995). Root exudates can also promote (phytosiderophores) metal uptake by plants and it can also lead to increased leaching of metals in the soil profile (Schulin et al., 1995; Alexander, 1977; Maywald and Weigel, 1997). This could explain the increased leaching of Cu in the camelina panel as compared to the control panel.

### ***3.2.12. P in surface runoff***

The dissolved P concentration (mg/L) in surface runoff in control panel was significantly higher than in the panel with camelina plants (Fig. 3-20). In samples taken

after 4 and 6 months after sowing of camelina, P concentration in the surface runoff was 28 and 9 times higher than in the camelina panel.

Total P concentration (mg/L) in surface runoff in control panel was significantly higher than in the panel with camelina plants (Fig. 3-21). In samples taken after 4 and 6 months after sowing of camelina, P concentration in the surface runoff was 55 and 30 times higher than in the camelina panel. The total P concentration in the surface runoff samples increased by more than twice as compared to dissolved P concentration in the same samples

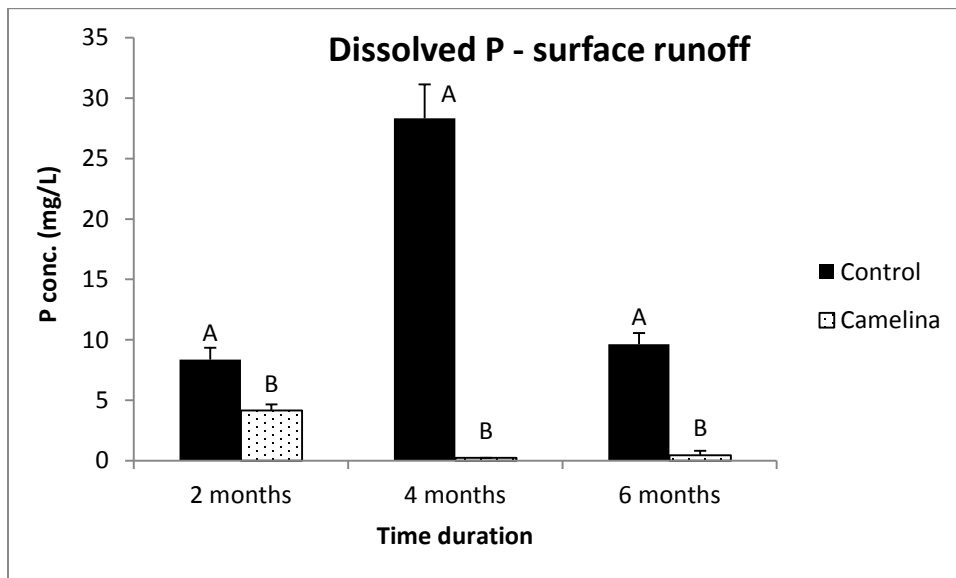


Fig. 3-20: Dissolved P (mg/L) in leachates in control and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

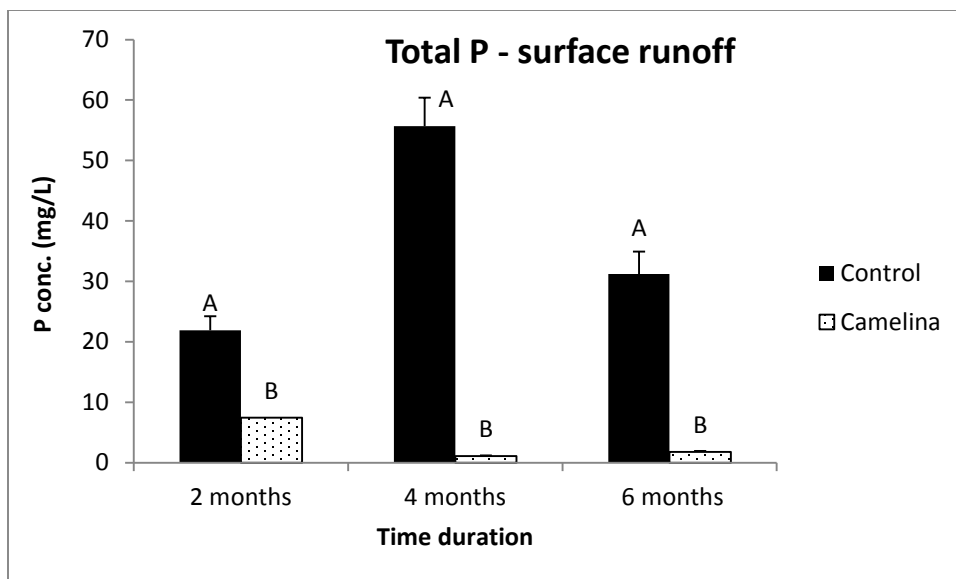


Fig. 3-21: Total P (mg/L) in leachates in control and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.13. P in leachates

Dissolved P concentration (mg/L) in leachates in the camelina panel was more as compared to control panel after two months of camelina sowing (Fig. 3-22). But, in the leachate samples taken after 4 months, the P concentration in the control panel was significantly more than camelina panel. The dissolved P concentration was almost same in control and camelina panels in the leachate samples taken after 6 months. Total P concentration (mg/L) in leachates in the camelina panel and control panel exhibited the same trend as in case of dissolved P concentration (Fig. 3-22). However, total P concentration increased slightly as compared to dissolved P concentration in the same samples.

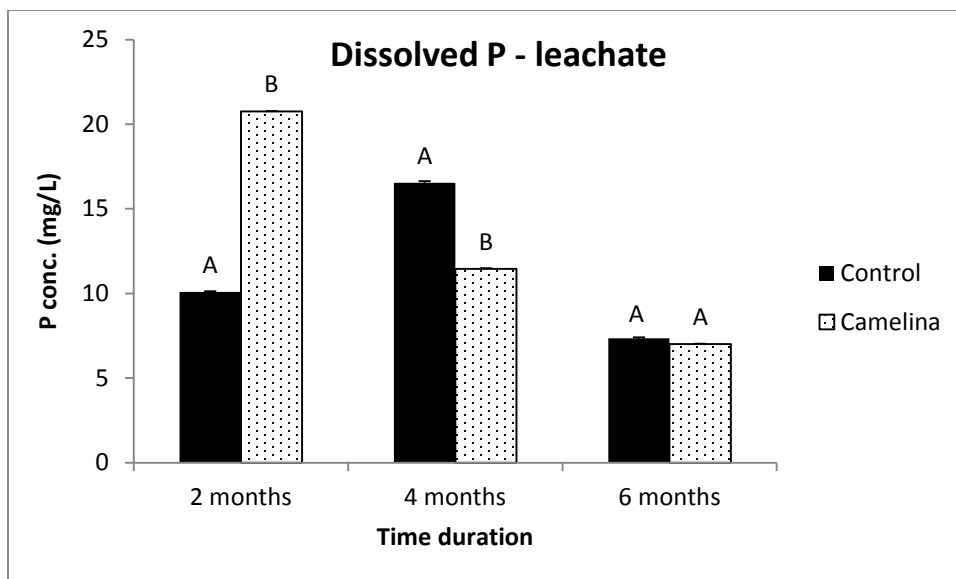


Fig. 3-22: Dissolved P (mg/L) in leachates in control and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

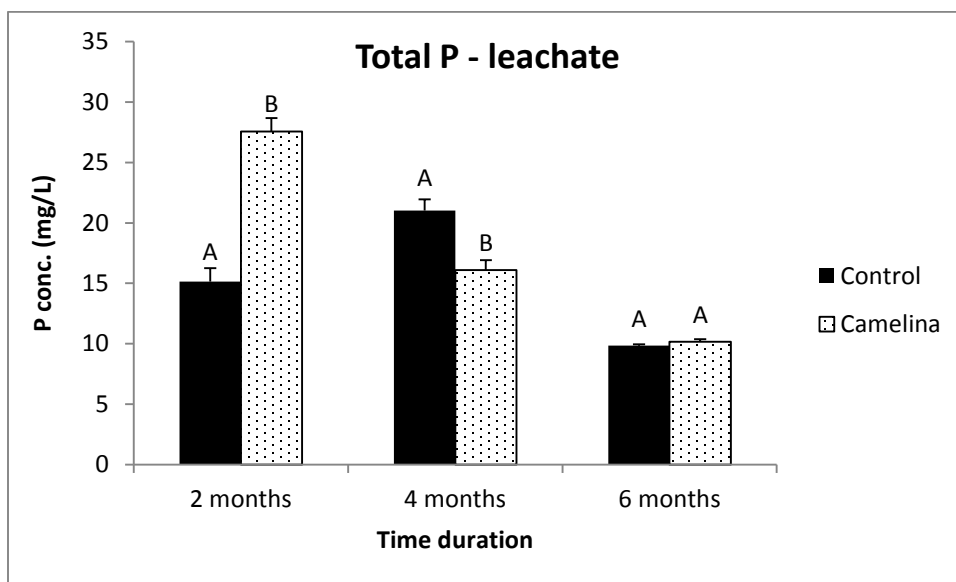


Fig. 3-23: Total P (mg/L) in leachates in control and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

### 3.2.14. Cu in camelina plants

The highest Cu concentration ( $\mu\text{g/g}$ ) in camelina plant parts (Fig. 3-18) was found in leaves (263  $\mu\text{g/g}$ ) followed by roots (205  $\mu\text{g/g}$ ), seeds (65  $\mu\text{g/g}$ ), pods (62  $\mu\text{g/kg}$ ) and stem (27  $\mu\text{g/g}$ ). The Cu concentration in leaves and roots was about four and three times more than Cu concentration in seeds and statistically significant from other plant parts (stem, pods, seeds).

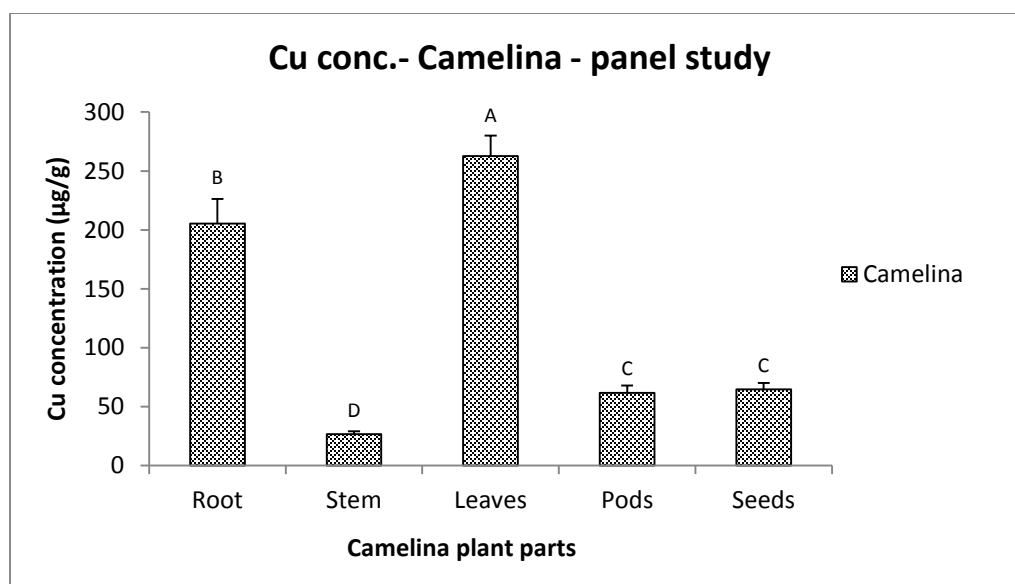


Fig. 3-24: Cu ( $\mu\text{g/g}$ ) in different parts of camelina plants during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

Various researchers have found that plants can alter chemical mobility and bioavailability of metals in the rhizosphere (Marschner, 1995; Hinsinger, 1998; McLaughlin et al., 1998). Roots also release soluble organic compounds (root exudates)

into the rhizosphere which can form complexes with Cu and can increase uptake of Cu by the plants (Mench et al., 1988; Treeby et al., 1989; Mench, 1990). Cu content in roots can be stored in the root cell walls (Cathala and Salsac, 1975) and can also move into the root and subsequently into the aerial parts of the plant (Marschner, 1995). Songa and co-workers in 2004 observed Cu concentrations in shoots of *Silene vulgaris* and *Elsholtzia splendens* as 262 mg/kg and 215 mg/kg, respectively when those plants were grown on Cu contaminated soil. The Cu concentrations found in shoots of camelina and field pennycress were well below the threshold of 1000 mg/kg which is commonly used to define Cu hyperaccumulation (Brooks, 1998). But, Cu concentrations in shoots were substantially higher than the toxicity threshold of 20–30 mg/kg (Marschner, 1995). Camelina and field pennycress have little potential for phytoextraction of Cu from contaminated soils but the high tolerance to Cu in the two plants can be used for phytostabilization of Cu contaminated soils.

### ***3.2.15. Cu in stamp sands***

At the end of the field simulation study, Cu concentration (mg/kg) in stamp sand of control panel was slightly less than the initial Cu concentration in the same panel at the start of the study (Fig. 3-19). Final Cu concentration in the control panel was also less than final Cu concentration in the camelina panel. But, the change in Cu concentration in the control panel was not statistically significant.



### 3.2.16. Mass balance of Cu in panel study

The total uptake of Cu by camelina plants in the panel was 9.2 mg (Table 3-6). In control and camelina panels, 90 and 84 mg of Cu leached in all the three leachates combined, respectively. The Cu in all surface runoff combined in control and camelina panels was 1786 and 123 mg, respectively.

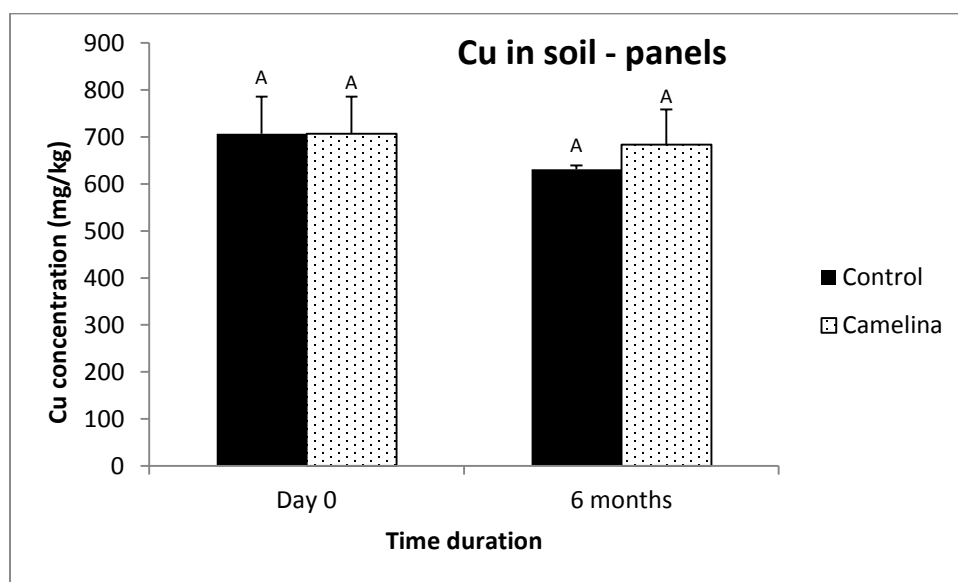


Fig. 3-25: Cu (mg/kg) in stamp sand in control (no plant) and camelina panels during the study period. Data is reported as mean  $\pm$  S.D. Means are compared by Tukey Kramer-HSD test ( $\alpha=0.05$ ). Levels not connected by the same letter are significantly different.

This demonstrates the loss of Cu in surface runoff in control panel which was quite high as compared to the camelina panel. But, the majority of Cu was still held in the stamp sands of control (76565 mg) and camelina (78545 mg) panels.

Table 3-6: Mass balance of Cu (mg) in the greenhouse panel study

	Roots (mg)	Stem (mg)	Leaves (mg)	Pods (mg)	Seeds (mg)	Total plant uptake (mg)	Total Cu (leachates; mg)	Total Cu (runoff; mg)	Total Cu (Soil; mg)
Control (No plant)	-	-	-	-	-	-	90	1786	76565
Camelina	2.48	1.90	3.84	0.34	0.63	9.2	84	123	78545

### 3.2.17. Oil content and quality of camelina seeds

The oil, protein and moisture content of camelina seeds was 20, 22.7 and 6.83%, respectively (Table 3-7).

Table 3-7: Percentage of oil, protein and moisture in camelina seeds. Data is expressed as mean (n=3)  $\pm$  standard deviation.

Oilseed crop	Oil (%)	Protein (%)	Moisture (%)
Camelina	20.0 $\pm$ 0.25	22.7 $\pm$ 0.58	6.83 $\pm$ 0.07

Moser and Vaughn (2010) reported the oil content of camelina seeds in their study as 30.5 %, and previous studies by Budin et al. (1995), Leonard (1998), Sawyer (2008) also found the oil content of camelina to be in that range. The oil content of rapeseed, soybean and sunflower was reported to be in the range 40-44%, 18-22% and 39-49% (Oil World Annual 2009). Peiretti and Meineri (2007) reported the protein content of the seed as 24.5% and was similar to that reported by Marquard and Kuhlmann (1986) (23.5 to 30.1%). The protein content of the plant is one of the qualitative

parameters that indicate the nutritional value of the crop. The composition of unsaturated fatty acids in the camelina consists of high percentage of  $\alpha$ -linolenic acid, which makes it suitable for ruminants when it is used as meal.

The fatty acid composition of camelina seeds (Fig. 3-26) shows high content of unsaturated fatty acids such as oleic acid (C18:1; 15.9%), linoleic acid (C18:2; 17.6%) and  $\alpha$ -linolenic acid (C18:3; 27.6%) and eicosenoic acid (C20:1; 13%), erucic acid (C22:1; 5.5%) comprising a total of 79.6% of the total fatty acids. The saturated fatty acids comprised of palmitic acid (C16:0; 7.1%), stearic acid (C18:0; 4.1%), arachidic acid (C20:0; 3.5%), behenic acid (C22:0; 1%) and lignoceric acid (C24:0; 1.2%).

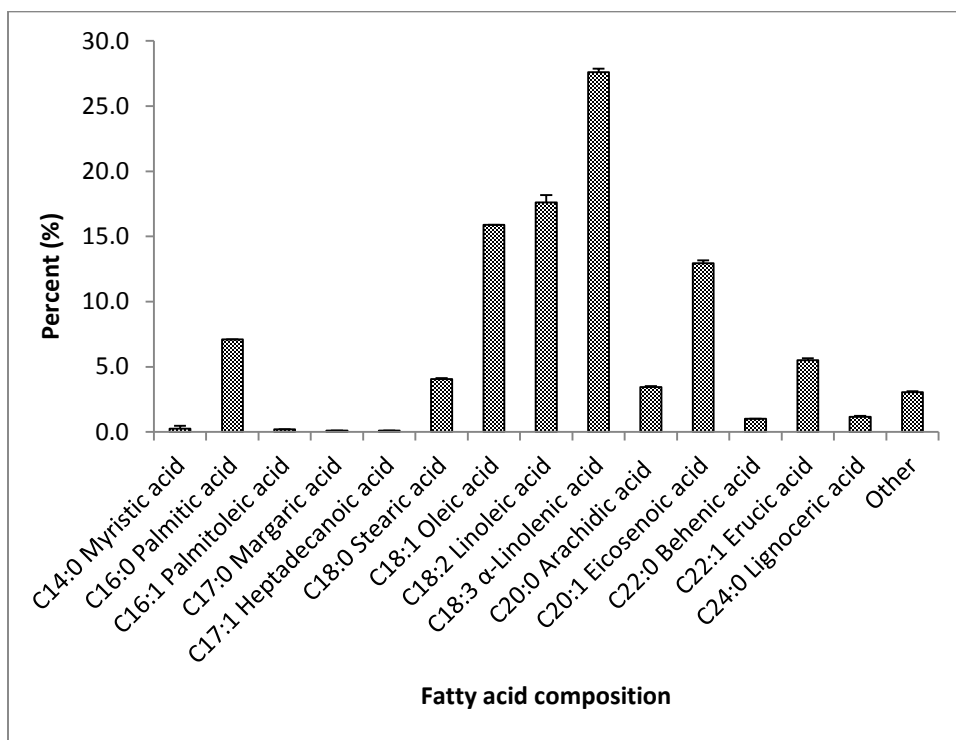


Fig. 3-26: Fatty acid composition (wt. % of extracted oil) of camelina seeds. Data is expressed as mean (n=2)  $\pm$  standard deviation.

Our results are in conformity with previous studies which found that the five fatty acids (16:0, 18:0, 18:1, 18:2, and 18:3) predominate in the major oilseed crops (Jaworski and Cahoon, 2003; Singh et al., 2005). Huber et al (2006) also observed that  $\alpha$ -linolenic acid comprised between 32 and 40% of the fatty acid composition of camelina oil. Other fatty acids in contents above 10% include linoleic, oleic, and eicosenoic acids. Moser and Vaughn (2010) also found that oil obtained from camelina seeds contained a high percentage of polyunsaturated fatty acids (54.3 %), with high content of  $\alpha$ -linolenic (32.6 %) and linoleic acid (19.6%). When plants are grown in environments with high metal, cellular modifications in the content and composition of fatty acids occur (Devi and Prasad 1999; Jemal et al. 2000; Bidar et al. 2008). Although, oil content (20%) of camelina seeds in our study decreased as compared to previous studies by Moser and Vaughn (2010), Budin et al. (1995), Leonard (1998), Sawyer (2008) which reported the camelina oil content to be 30%, but the fatty acid composition remained in conformity with previous studies.

Park et al (2015) observed that there was a decrease in the unsaturated fatty acid amount and composition under Cd, Co, Zn, Pb stress both in the wild type and transgenic camelina. But, Park et al. (2015) observed that the decrease in the total fatty acid content and unsaturated fatty acids was less in transgenic camelina than wild type. Oil content and fatty acid composition have always determined if an oilseed crop can be used for making biofuel on an industrial scale (Rodríguez-Rodríguez et al. 2013). The variations in the fatty acid composition of the seed oil arise not only due to difference in plant

cultivars but also due to different geographical regions and different growing conditions (Abramovic and Abram, 2005; Zubr, 2003).

### 3.3 Conclusions

In the greenhouse column study, Cu concentration in camelina and field pennycress was maximum in leaves closely followed by roots and then in stem, pods and seeds. Cu and P concentration in the leachates was quite less in the first two months but increased in the third month and decreased thereafter subsequently in the later months. However, at the end of the greenhouse column study, Cu was mainly present in stamp sand and there was very little uptake (mass) of Cu in the plant parts of camelina and field pennycress. The turbidity in the leachates could not act as a proxy for the measurement of stamp sand erosion. Although, the measurement of turbidity and total suspended solids in the surface runoff in a panel could measure stamp sand erosion. In the greenhouse panel study which simulated field study, camelina decreased stamp sand erosion significantly in the surface runoff as compared to the control panel with no plants during the study period. Cu concentration also decreased significantly in surface runoff from the camelina panel as compared to control. Cu concentration in camelina parts was maximum in leaves followed by roots. There was negligible amount of Cu in the camelina seeds which was essential for the camelina seeds to be used for making biodiesel. Camelina seeds contained 20 and 22.7% oil and protein content, respectively. The fatty acid composition of camelina seeds contained the maximum contents of unsaturated fatty acids (oleic, linoleic,  $\alpha$ -linolenic and eicosenoic acid). The composition of unsaturated fatty acids did

not differ too much from the previous studies done on uncontaminated agricultural soils. Camelina grown on contaminated stamp sands amended with compost not only significantly reduced stamp sand erosion but also served as a potential feedstock for biodiesel owing to high oil content and quality of camelina seeds. This model can be used on other marginal lands for their restoration/ stabilization and producing biofuel feedstock which would also avoid the food-fuel conflict that arises by growing biofuel feedstock on agricultural lands.

### 3.4 References

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## **CHAPTER 4**

### **EFFECT OF THE REDUCTION IN STAMP SAND EROSION AND BIOFUEL FEEDSTOCK PRODUCTION ON THE LOCAL COMMUNITY IN TORCH LAKE, MI: A DOOR TO DOOR SURVEY**

#### Abstract

Large scale mining activities occurred during the late 19<sup>th</sup> to early 20<sup>th</sup> century in the Upper Peninsula of Michigan. That mining has resulted in several contaminated sites. Several million tons of residues were formed due to mining. Those residues are called “stamp sands”. Stamp sands were made by crushing rocks with copper in them. These stamp sands eroded into Lake Superior, and other lakes. The copper polluted sands are being eroded back into the lakes. This affects the lake bottom community. In 2014-15, I conducted a research study to grow native oil seed crops. Oil seed crops such as “camelina” and “field pennycress” reduce soil erosion. The seeds from these crops can also serve as a source of biofuel. This study helps in finding new ways for growing these crops on marginal lands. These crops prevent soil erosion and also provide a source of biofuel. Torch Lake in the Upper Peninsula can serve as a model for this solution. I did a public opinion survey of the community of Torch Lake Township to gauge the views of the local residents about starting our project there. I went door to door for administering the survey questionnaire in July-August, 2015. The participants filled out a survey questionnaire given by me. In one household, not more than one adult filled out the

survey questionnaire. It took 10-15 minutes to fill in the survey questionnaire. The responses would help us in designing a better research project for Torch Lake. I also hoped to gauge the views of the local residents about the environment.

#### **4. Introduction**

Extensive mining activities during the late 19<sup>th</sup> and early 20<sup>th</sup> centuries in the Upper Peninsula, Michigan have resulted in copper (Cu) contamination of the environment. Several million metric tons of mine tailings were generated during the peak of Cu mining activities in this region. These tailings are called “stamp sands” because they were generated by crushing native Cu containing rocks via a process called stamping. The stamp sands were discharged into Lake Superior, and other interior lakes that are its offshoots. Torch Lake is part of the Keweenaw waterway in the Upper Peninsula of Michigan and connects to Lake Superior via Portage Lake. Torch Lake was filled with about 200 million tons of stamp sands from the copper industry from 1868 to 1968, filling about 20% of the lake volume (Cusack and Mihelcic 1999; Weston 2007). The mining companies dredged the sediments and dumped them on lake shores from early to mid-1900s for copper reclamation activities converting these areas into vast, fallow lands (Weston 2007).

In 1983, the Michigan Department of Public Health (MDPH) issued a fish consumption advisory for sauger and walleye because of the high incidence of fish tumors (MDPH 1983; MDNR 1987). In 1984, the hazard ranking system was applied to



the Torch Lake site as Cu concentrations were significantly above background levels (US EPA 1989). In 1986, 14 areas within the Keweenaw Peninsula of Houghton County, Michigan were designated as a Superfund site and have been commonly referred to as the Torch Lake Superfund site (US EPA 1986). The US EPA decided to establish a vegetative cover over the stamp sands surrounding the lake as part of the remediation work to delist the site (MDEQ 2007). But, the vegetation has not been able to grow uniformly over the stamp sands and there are numerous bare patches where there is no plant growth at all. Native vegetation could not grow properly because of Cu toxicity, and the nutrient-poor quality of stamp stands, which texturally lack water-holding capacity. Now, the Cu contaminated stamp sands are being eroded back into the lakes, thus affecting the aquatic population again. There were signs installed in June 2015 on the Hubbell beach on the Torch Lake shoreline about potential hazards of high concentration of heavy metals in the stamp sands (TLT 2015). It is understood that unless the stamp sands are fertilized to the point of sustaining vegetation growth, the problem with erosion and water quality degradation will continue.

Biosolids are commonly used as organic fertilizers and are a sustainable and good source of nutrients, which help in the growth of plants, and also improve the soils' physical and microbiological properties (Boyl and Paul 1989; USEPA 1995; Su and Wong 2003). Biosolids can serve to restore metal affected sites by providing essential nutrients to support vigorous plant cover on the mine tailings (Brown et al. 2003). Biosolids have been used to successfully restore mine lands for 25 years or more

(Haering et al. 2000; Sopper 1993). Composts have been historically used as another slow-release, organic source of fertilizer. The establishment of plant cover on stamp sands will reduce the potential of erosion and contaminant transfer into the Torch Lake.

During the past several decades, worldwide petroleum consumption has increased tremendously due to the growth of human population and industrialization, which has resulted in depletion of fossil fuel reserves and an increase in the price of petroleum. The transport sector is heavily dependent on petroleum derived fuels. Therefore, there is a great need for diesel fuel substitution all over the world with a clean, renewable fuel such as biodiesel (Balat and Balat, 2010). Biodiesel is an alternative fuel composed of mono-alkyl esters of long-chain fatty acids and is prepared from vegetable oils or animal fats by a process known as transesterification. Biodiesel has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). Biodiesel possesses significant technical advantages over petrodiesel, such as derivation from renewable feedstocks, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, superior flash point and biodegradability, reduced toxicity, as well as a reduction in exhaust emissions (Mittelbach and Remschmidt, 2004; Knothe et al., 2005; McCormick et al., 2006; Moser, 2009a). Feedstocks for biodiesel production vary considerably with location according to climate and availability. Generally, the most abundant lipid in a particular region is the most common feedstock. Thus, rapeseed oil is predominantly used in Europe, palm oil predominates in Southeast Asia, and soybean oil and animal fats are primarily used in the United States, Brazil and Argentina (Mittelbach

and Remschmidt, 2004; Knothe et al., 2005; Moser, 2009a). But, the high cost of commodity vegetable oils, such as soybean oil in the United States, represents a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder, 2007; Retka-Schill, 2008a). Presently, feedstock acquisition accounts for up to 85% of biodiesel production costs (Paulson and Ginder, 2007; Retka-Schill, 2008a). However, many of these oils are quite expensive and also have competing food-related uses. Consequently, the development of alternative feedstock for biodiesel production that meet all or most of the following criteria has attracted considerable research attention: high oil content, low agricultural inputs, favorable fatty acid composition, compatibility with existing farm equipment and infrastructure, production in a sustainable fashion in off-season or in agriculturally undesirable lands, definable growth seasons, and uniform seed maturation rates. Field pennycress (*Thlaspi arvense*) (Moser et al., 2009a) and camelina (*Camelina sativa*) (Moser and Vaughn, 2010) are recent examples of crops which are source of feedstock oils for biodiesel that meet at least a majority of the above criteria.

A survey questionnaire was designed to do a door to door survey of the Torch Lake Township in Upper Peninsula of Michigan in order to:

1. Learn the views of the local community about initiating our research project near Torch Lake.
2. Learn the views of the local community about local and global environmental issues.

A letter of agreement seeking permission for the door to door survey from the Torch Lake Township was obtained (appendix B). Necessary training requirements (CITI certificate) were obtained by the PI (Virinder Sidhu) and co-PI/faculty sponsor for the survey (Dr Yong Wang) before filing the application at the IRB (Institutional Review Board) office of Montclair State University. The survey was approved by the IRB (IRB Protocol# 001526; appendix A).

#### ***4.1 Materials and Methods***

##### ***4.1.1. Survey methodology and execution***

A pre-notification letter (appendix C) for the survey was printed in the township's newsletter and mailed to the Torch Lake Township residents by the township administration in June, 2015 informing them of the upcoming survey. A random sample of 373 households out of a total of 771 households (US Census Bureau, 2012) within the boundaries of Torch Lake Township in Upper Peninsula of Michigan were attempted to be contacted by me over a period of 30 days in July-August, 2015. I visited 373 households so as to complete a survey with one eligible participant at each address. A participant had to be a resident of the Torch Lake Township and 18 years or above in age in order to participate in the study. Of the 373 houses visited, the door was answered by an individual in 119 houses; an individual in 38 houses refused to complete the survey questionnaire; an individual in 81 houses completed the survey questionnaire. There were 26 houses that were found to be locked with locks hanging outside the houses and with

no visible individuals in the house. The occupants may have been traveling or would have sold the houses or had multiple houses or houses may have been abandoned. The response rate of the survey was 68.1% ( $81/119 \times 100$ ). All the participants signed a consent form (appendix D) before completing the survey questionnaire. One copy of the consent form was given to the participant to keep and one copy of consent form signed by the participant was returned to me.

A twenty six item survey questionnaire (appendix E) was developed in accordance with guidelines proposed by Dillman et al., 2009. Thirteen variables were designed about the local environment of the Torch Lake and were put first in the survey questionnaire. After that, four variables were regarding global environment (climate change). The last part of questionnaire required respondents to respond to seven demographic variables (gender, age, education attainment, annual household income, race and duration of stay in the township). At the end of the survey questionnaire, two variables relating to political and religious inclination were placed.

#### ***4.1.2 Statistical analyses***

The data were statistically analyzed using the statistical software JMP version 10 (SAS 2012). Contingency data analysis was done for gender and educational attainment. Factor analysis (maximum likelihood/Varimax) of variables relating to the global environment and local environment in Torch Lake, MI was done in order to decrease the number of variables that corresponded to the global environment and local environment,

respectively. The chi square test for significance ( $p < 0.0001$ ) was used to test the significance of variables in factor analysis.

Multiple regression of climate change, local environment and demographic variables was carried out. The two variables each from climate change and local environment variables shortlisted after doing their factor analysis were used to do multiple regression. Four fit model scenarios were executed as fit model 1, 2, 3 and 4. In fit model 1, multiple regression was done with “climate change is real as Y/dependent variable” and “The project includes two native oilseed crops (Camelina and Field Pennycress), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.” as X/independent variable. In fit model 2, multiple regression was done with “climate change is a natural occurring process as Y/dependent variable” and “I am concerned with high copper levels in the Torch Lake” as X/independent variable”. In fit model 3, multiple regression was done with “climate change is real as Y/dependent variable” and “I am concerned with high copper levels in the Torch Lake” as X/independent variable”. In fit model 4, multiple regression was done with “climate change is a natural occurring process as Y/dependent variable” and “The project includes two native oilseed crops (Camelina and Field Pennycress), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.” as X/independent variable. Demographic variables were used as independent variables in each model. The level of significance was set at  $p < 0.1000$ .

## 4.2 Results and Discussion

### *4.2.1. Analysis of responses by percentages*

Fifty eight percent of the respondents were male and forty two percent of the respondents were female (Table 4-1). Forty one percent of the respondents said they had a college degree and of which fifty two said they had bachelor degrees. Fifty six percent of the respondents said that they had an annual household income of \$45,000 and more and twenty nine percent of the respondents said that they had more than \$75,000 annual household income. Ninety nine percent of the respondents identified their race as white. Eighty percent of the respondents said that they considered themselves as religious.

Almost all the respondents (99%) said that they valued the environment. Ninety one percent of the respondents said that they knew about high copper (Cu) concentration in Torch Lake and ninety five percent of the respondents agreed that they were concerned about it. Ninety three percent of the respondents said that they knew about high Cu concentration in the stamp sand around Torch Lake. Eighty nine percent of the respondents agreed that they are concerned with erosion of soil with high Cu concentration into the Torch Lake. Ninety seven percent of the respondents agreed that they will support a scientific research project to reduce erosion of stamp sands with high Cu concentration into Torch Lake and ninety seven percent respondents agreed that it will benefit the water quality of Torch Lake. Ninety seven percent of the respondents also agreed that they will support our research project for improving the water quality of

Torch Lake. Ninety two percent of the respondents agreed that revenue earned from the sale of oilseeds can benefit the local community and ninety four percent respondents agreed that it can also lead to job creation in the local community. Ninety three percent respondents agreed that our research project can also improve the recreation area around the Torch Lake. Sixty eight percent of the respondents agreed that government (federal, state and local) should undertake such a research project around Torch Lake whereas twenty percent of the respondents said they preferred public private partnership and only ten percent of the respondents preferred private institutions for undertaking such a project in their community. Ninety three percent of the respondents agreed that nonfood crops grown on marginal lands can be used for producing biofuel feedstock.

Eighty three percent of the respondents agreed that climate change is real and seventy eight percent of the respondents agreed that it is caused by the anthropogenic activities. However, eighty nine percent of the respondents also agreed that climate change is a natural occurring phenomenon. Even so, a large majority of respondents (87%) agreed that we need to protect our planet from climate change.

#### ***4.2.2. Effect of gender on variation in responses***

Fifty two of the respondents were male and forty two of the respondents were female (Table 4-1). A contingency table analysis of the responses was done to analyze the effect of gender (male or female) on the responses (Table 4-2). Ninety one percent of both male and female respondents knew about the high levels of Cu in the Torch Lake.



Ninety one percent of male and ninety four percent of female respondents knew about high levels of Cu in the soil around Torch Lake.

Table 4-1: Analysis of survey responses by percentages

Question	Options*	%	Question	Options	%	Question	Options	%
1	1	99		3	21	20	1	41
	2	1		4	4		2	59
2	1	91		5	2	21	1	21
	2	9		6	1		2	52
3	1	93	12	1	29		3	27
	2	7		2	17		22	1
4	1	89		3	22		2	22
	2	11		4	10		3	15
5	1	37		5	20		4	18
	2	32		6	2		5	9
	3	26	13	1	44		6	29
	4	4		2	18		23	1
	6	1		3	21		1	1
	1	58		4	10		6	1
6	2	19		5	6	25	1	21
	3	20		6	1		2	26
	4	1	14	1	25		3	11
	5	2		2	34		4	18
7	1	64		3	19		5	24
	2	15		4	13		26	1
	3	18		5	5		2	20
	4	1		6	5			
	5	3	15	1	27			
	1	56		2	35			
8	2	21		3	27			
	3	20		4	7			
	4	2		5	4			
	5	1		1	40			
9	1	41		2	23			
	2	30		3	24			
	3	21		4	10			
	4	4		5	1			
	5	4		6	3			

10	1	42	17	1	32			
	2	30		2	34			
	3	22		3	27			
	4	5		4	6			
	5	1		5	1			
11	1	58	18	1	58			
	2	14		2	42			

\*- Question 1, 2, 3, 4, 20, 26; 1-Yes, 2-No. For question 5-17; 1-Strongly agree, 2-Somewhat agree, 3-Agree, 4-Disagree, 5-Somewhat disagree, 6-Strongly disagree

Table 4-2: Contingency table data analysis by gender (values are in percentage)

Question	Gender	1	2	3	4	5	6
Q2	M <sup>^</sup>	91	9				
	F <sup>#</sup>	91	9				
Q3	M	91	9				
	F	94	6				
Q4	M	87	13				
	F	91	9				
Q5	M	34	32	30	2	2	
	F	41	32	21	6	0	
Q6	M	60	19	19	0	2	
	F	56	18	21	3	3	
Q7	M	41	33	17	7	2	
	F	18	36	39	6	0	
Q8	M	57	21	19	0	2	
	F	53	21	21	6	0	
Q9	M	41	30	22	2	4	
	F	41	29	21	6	3	
Q10	M	42	29	20	7	2	
	F	41	32	24	3	0	
Q11	M	64	6	19	4	4	2
	F	50	24	24	3	0	0
Q13	M	38	19	17	13	11	2
	F	52	15	27	6	0	0
Q14	M	28	32	19	11	4	6
	F	21	36	18	15	6	3
Q15	M	30	34	28	6	2	
	F	24	35	26	9	6	
Q16	M	36	26	21	11	2	4

	F	45	18	27	9	0	0
Q17	M <sup>\$</sup>	41	33	17	7	2	
	F <sup>\$</sup>	18	36	39	6	0	

^M- Male, #F-Female \*- Question 1, 2, 3, 4, 20, 26; 1-Yes, 2-No. For question 5-17; 1-Strongly agree, 2-Somewhat agree, 3-Agree, 4-Disagree, 5-Somewhat disagree, 6-Strongly disagree

\$ - statistically significant (p=0.0888; or p <0.10)

Ninety six percent of male and ninety four percent of female respondents agreed that they were concerned by the Cu levels in the Torch Lake. Ninety eight percent of male and ninety five percent of female respondents said that they will support a project to reduce stamp sand erosion in to the Torch Lake. Ninety one percent of male and ninety three percent of female respondents agreed water quality can be improved by reducing the stamp sand erosion in to the Torch Lake. Ninety seven percent of male and ninety five percent of female respondents supported our project to reduce stamp sand erosion in to the Torch Lake and also produce biofuel feedstock. Ninety three percent of male and eighty one percent of female respondents agreed that the potential revenue that can be generated from the sale of oilseeds for the production of biofuel in their community with the implementation of our project. Ninety one percent of male and ninety seven percent of female respondents agreed that new jobs can be created in their community with the implementation of our project will benefit the community. Eight nine percent of male and ninety eight percent of female respondents agreed that Torch Lake can be used as a recreational area after the implementation of our project. Ninety one percent of male and ninety three percent of female respondents agreed that non-food crops can be grown on

marginal lands to produce biofuel feedstock. This variable was statistically significant in the contingency analysis ( $p=0.0888$ ).

About the global environmental issue of climate change, seventy four percent of male and ninety four percent of female respondents agreed that climate change is real. Seventy nine percent of male and seventy five percent of female respondents agreed that climate change is caused by the activities of people. But, ninety two percent of male and eighty five percent of female respondents also agreed that climate change is a natural occurring phenomenon. Eighty three percent of male and ninety percent of female respondents agreed that we need to protect our planet from climate change.

#### ***4.2.3. Effect of education on variation in responses***

Forty one percent of respondents said they had a college degree and of which fifty two percent respondents said they had bachelor degrees. A contingency analysis of the responses was done to analyze the effect of education (presence or absence of college degrees; Table 4-3) on the responses. The respondents knew about the same about the high levels of Cu in the Torch Lake and in the soil around Torch Lake irrespective of presence or absence of college degrees. But, ninety four percent of respondents who had college education acknowledged that stamp sand erosion into the Torch Lake is a concern where as it were eighty five percent in case of respondents who didn't have college education. Ninety nine percent of college educated and ninety one percent of non-college educated respondents said that they were concerned with the Cu levels in Torch lake All

the respondents who were college educated agreed that they will support a project to reduce stamp sand erosion into the Torch Lake where as it was ninety four percent in case of respondents who were non-college educated. All the respondents agreed that water quality can be improved by reducing the stamp sand erosion in to the Torch Lake irrespective of college education. All the respondents who were college educated supported our project where as it was ninety four percent in case of respondents who were non-college educated. Ninety seven percent of respondents who were college educated agreed that to the potential revenue that can be generated from the sale of oilseeds for the production of biofuel in their community with the implementation of our project whereas ninety percent of non-college educated respondents agreed to that notion. This variable was statistically significant ( $p=0.0438$ ) in the contingency analysis. Ninety seven percent of college educated respondents and ninety one percent of non-college educated respondents agreed that new jobs can be created in their community with the implementation of our project. Ninety one percent of college educated and ninety four percent of non-college educated respondents agreed that Torch Lake can be used as a recreational area after the implementation of our project.

About the global environmental issue of climate change, eighty four percent of college educated and eighty one percent of non-college educated respondents agreed that climate change is real. Ninety percent of college educated and sixty nine percent of non-college educated respondents agreed that climate change is caused by the activities of people. Ninety percent of college educated and eighty seven percent of non-college

educated respondents also agreed that climate change is a natural occurring phenomenon.

But, eighty seven percent of respondents, irrespective of college degree, agreed that we need to protect our planet from climate change.

Table 4-3: Contingency data analysis by education (college degree)

		1	2	3	4	5	6
Q2	Y <sup>^</sup>	91	9				
	N <sup>#</sup>	92	8				
Q3	Y	91	9				
	N	94	6				
Q4	Y	94	6				
	N	85	15				
Q5	Y	45	30	24	0	0	
	N	31	33	27	6	2	
Q6	Y	61	21	18	0	0	
	N	56	17	21	2	4	
Q7	Y	66	15	19	0	0	
	N	63	15	17	2	4	
Q8	Y	58	27	15	0	0	
	N	54	17	23	4	2	
Q9	Y <sup>\$</sup>	59	19	19	3	0	
	N <sup>\$</sup>	29	38	23	4	6	
Q10	Y	48	26	23	3	0	
	N	38	33	21	6	2	
Q11	Y	64	12	15	6	0	3
	N	54	15	25	2	4	0
Q13	Y	45	21	18	12	3	0
	N	43	15	23	9	9	2
Q14	Y	24	42	24	6	0	3
	N	26	28	15	17	9	6
Q15	Y	27	42	21	9	0	
	N	27	29	31	6	6	
Q16	Y	45	24	18	12	0	0
	N	36	21	28	9	2	4
Q17	Y	39	27	27	6	0	
	N	26	39	26	7	2	

^Y-Yes, #N-No \*- Question 1, 2, 3, 4, 20, 26; 1-Yes, 2-No. For question 5-17; 1-Strongly agree, 2-Somewhat agree, 3-Agree, 4-Disagree, 5-Somewhat disagree, 6-Strongly disagree

\$ - statistically significant ( $p=0.0438$  or  $p<0.10$ )

#### ***4.2.4. Factor analysis of variables relating to climate change***

Factor analysis (maximum likelihood/Varimax) of four variables relating to climate change was done in order to decrease the number of variables that corresponded to climate change (Table 4-4). The chi square test for significance ( $p<0.0001$ ) found at least one common factor for the four variables and found that two factors were sufficient. The variable, “climate change is real” with highest value (0.88725) in factor 1 and another variable, “climate change is a natural occurring process” with highest value in factor 2 (0.587613) were sufficient to represent variables relating to climate change.

Table 4-4: Factor analysis of climate change variables

Variable relating to climate change	Factor 1	Factor 2
Climate change is real	<b>0.88725</b>	-0.06382
Climate change is caused by the activities of people	0.736618	-0.33018
Climate change is a natural occurring process	-0.07606	<b>0.587613</b>
We need to protect our planet from climate change	0.786833	-0.06073

#### ***4.2.5. Factor analysis of variables relating to local environment***

Factor analysis (maximum likelihood/Varimax) of variables relating to the local environment in Torch Lake, MI was done in order to decrease the number of variables that corresponded to the local environment (Table 4-5). The chi square test for

significance ( $p < 0.0001$ ) found at least one common factor for the four variables and found that two factors were sufficient. The variable, “the project includes two native oilseed crops (camelina and field pennycress) which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project” with highest value (0.888759) in factor 1 and another variable, “I am concerned with high copper levels in the Torch Lake” with highest value in factor 2 (0.762288) were sufficient to represent variables relating to the local environment.

Table 4-5: Factor analysis of variables relating to local environment in Torch Lake, MI

Variables relating to local environment	Factor 1	Factor 2
I am concerned with high copper levels in the Torch Lake	0.647238	<b>0.762288</b>
I would support a scientific project to reduce erosion of soil with high copper levels into Torch Lake	0.874387	0.128787
The reduction of erosion of soil with high copper levels into Torch Lake will be beneficial for water quality	0.776167	0.258477
The project includes two native oilseed crops (“Camelina” and “Field Pennycress”), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.	<b>0.888759</b>	0.01537
The revenue earned from the sale of oilseeds of Camelina and Field Pennycress will benefit your community and the oilseeds can be used to produce biodiesel	0.745063	-0.01793
This project can lead to the creation of jobs in the Torch Lake community	0.806549	0.039481
This project can lead to the greater use of Torch Lake as a recreational area	0.706538	0.199493
Federal agency (US EPA) should undertake such a project in your township?	0	0
State agency (MDEQ) should undertake such a project in your township?	0	0
Local government (Torch Lake Township) should undertake such a project in your township?	0	0
Private company should undertake such a project in your township?	0	0



Public-Private partnership should undertake such a project in your township?	0	0
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#### ***4.2.6. Multiple regression of climate change, local environment and demographic variables***

Multiple regression of climate change, local environment and demographic variables was carried out. The two variables each from climate change and local environment variables shortlisted after doing their factor analysis were used to do multiple regression. Four fit model scenarios were executed as fit model 1, 2, 3 and 4. In fit model 1 (Table 4-6), multiple regression was done with “climate change is real as Y/dependent variable” and “The project includes two native oilseed crops (Camelina and Field Pennycress), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.” as X/independent variable. The demographic variables were used as independent variables. The variable relating to college education (BA/BS) was significant ( $p= 0.0262$ ) and positively correlated with the dependent variable. The annual household income of \$30,000-44,999 was also significant ( $p=0.0299$ ) and positively correlated with the dependent variable.

In fit model 2 (Table 4-7), multiple regression was done with “climate change is a natural occurring process as Y/dependent variable” and “I am concerned with high copper levels in the Torch Lake” as X/independent variable”. The demographic variables

were used as independent variables. There was no significant correlation ( $p < 0.1000$ ) between the dependent and variables in this model.

Table 4-6: Multiple regression (Fit Model 1) of climate change (climate change is real =Y), local environment and demographic variables

Term	Estimate	Prob> t
Intercept	4.160849	0.0341
The project includes two native oilseed crops (Camelina and Field Pennycress), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.	-0.08835	0.7878
What is your gender?[1]	0.329445	0.2624
What is your age?	-0.02974	0.0959
If you answered yes to question 20, what is the highest college degree that you have?[2-1]	2.38399	0.0262*
If you answered yes to question 20, what is the highest college degree that you have?[3-2]	-0.65816	0.3899
If you answered yes to question 20, what is the highest college degree that you have?[4-3]	-0.49246	0.7772
In which of these groups did your total household income for last year fall?[2-1]	-4.47831	0.0709
In which of these groups did your total household income for last year fall?[3-2]	3.015557	0.0299*
In which of these groups did your total household income for last year fall?[4-3]	-2.0602	0.0874
In which of these groups did your total household income for last year fall?[5-4]	0.828846	0.5528
In which of these groups did your total household income for last year fall?[6-5]	0.198081	0.8697
How long have you been living in Torch Lake Township?	-0.00801	0.6439
Whom did you vote in the last Presidential elections?[1]	0.956556	0.2092
Whom did you vote in the last Presidential elections?[2]	1.597118	0.0093*
Whom did you vote in the last Presidential elections?[3]	-0.07791	0.8854
Whom did you vote in the last Presidential elections?[4]	-1.75752	0.113
Do you consider yourself religious?[1]	0.104146	0.7739

\* Significant ( $p < 0.1000$ )

Table 4-7: Multiple regression (Fit Model 2) of climate change (climate change is a natural occurring process=Y), local environment and demographic variables

Term	Estimate	Prob> t
Intercept	4.040337	0.0838
I am concerned with high copper levels in the Torch Lake	0.032395	0.9352
What is your gender?[1]	-0.31157	0.4036
What is your age?	-0.02921	0.1739
If you answered yes to question 20, what is the highest college degree that you have?[2-1]	0.638693	0.5986
If you answered yes to question 20, what is the highest college degree that you have?[3-2]	-0.13096	0.8868
If you answered yes to question 20, what is the highest college degree that you have?[4-3]	-1.17602	0.5748
In which of these groups did your total household income for last year fall?[2-1]	-0.95787	0.7326
In which of these groups did your total household income for last year fall?[3-2]	-0.15264	0.9209
In which of these groups did your total household income for last year fall?[4-3]	-0.3528	0.797
In which of these groups did your total household income for last year fall?[5-4]	-0.00429	0.9979
In which of these groups did your total household income for last year fall?[6-5]	-0.14251	0.9221
How long have you been living in Torch Lake Township?	0.013985	0.5249
Whom did you vote in the last Presidential elections?[1]	0.80372	0.3815
Whom did you vote in the last Presidential elections?[2]	0.400817	0.5061
Whom did you vote in the last Presidential elections?[3]	-0.16808	0.8059
Whom did you vote in the last Presidential elections?[4]	-0.98593	0.4447
Do you consider yourself religious?[1]	0.080268	0.8575

In fit model 3 (Table 4-8), multiple regression was done with “climate change is real as Y/dependent variable” and “I am concerned with high copper levels in the Torch Lake” as X/independent variable”. The demographic variables were used as independent variables. The variable relating to college education (BA/BS) was significant (p= 0.027)

and positively correlated with the dependent variable. The annual household income of \$30,000-44,999 was also significant ( $p=0.0303$ ) and positively correlated with the dependent variable.

Table 4-8: Multiple regression (Fit Model 3) of climate change (climate change is real=Y), local environment and demographic variables

Climate change is real = Y			
Term		Estimate	Prob> t
Intercept		4.22052	0.0329
I am concerned with high copper levels in the Torch Lake		-0.11721	0.7166
What is your gender?[1]		0.368703	0.2308
What is your age?		-0.03004	0.0925
If you answered yes to question 20, what is the highest college degree that you have?[2-1]		2.490592	0.027*
If you answered yes to question 20, what is the highest college degree that you have?[3-2]		-0.63071	0.405
If you answered yes to question 20, what is the highest college degree that you have?[4-3]		-0.48781	0.7715
In which of these groups did your total household income for last year fall?[2-1]		-4.5723	0.0667
In which of these groups did your total household income for last year fall?[3-2]		3.094764	0.0303*
In which of these groups did your total household income for last year fall?[4-3]		-2.09637	0.0828
In which of these groups did your total household income for last year fall?[5-4]		0.825831	0.5356
In which of these groups did your total household income for last year fall?[6-5]		0.213605	0.856
How long have you been living in Torch Lake Township?		-0.00961	0.587
Whom did you vote in the last Presidential elections?[1]		0.966657	0.2034
Whom did you vote in the last Presidential elections?[2]		1.560622	0.0086*
Whom did you vote in the last Presidential elections?[3]		-0.1087	0.8437
Whom did you vote in the last Presidential elections?[4]		-1.67576	0.1265
Do you consider yourself religious?[1]		0.099536	0.7828

\* Significant ( $p<0.1000$ )

In fit model 4 (Table 4-9), multiple regression was done with “climate change is a natural occurring process as Y/dependent variable” and “The project includes two native oilseed crops (Camelina and Field Pennycress), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.” as X/independent variable. The demographic variables were used as independent variables. There was no significant correlation ( $p < 0.1000$ ) between the dependent and variables in this model.

Table 4-9: Multiple regression (Fit Model 4) of climate change (climate change is a natural occurring process=Y), local environment and demographic variables

Climate change is a natural occurring process = Y		
Term	Estimate	Prob> t
Intercept	4.155516	0.0742
The project includes two native oilseed crops (“Camelina” and “Field Pennycress”), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked	-0.05769	0.8866
What is your gender?[1]	-0.30705	0.3901
What is your age?	-0.02932	0.1716
If you answered yes to question 20, what is the highest college degree that you have?[2-1]	0.675573	0.5568
If you answered yes to question 20, what is the highest college degree that you have?[3-2]	-0.14416	0.8762
If you answered yes to question 20, what is the highest college degree that you have?[4-3]	-1.33162	0.5388
In which of these groups did your total household income for last year fall?[2-1]	-0.97858	0.7254
In which of these groups did your total household income for last year fall?[3-2]	-0.07096	0.9619
In which of these groups did your total household income for last year fall?[4-3]	-0.44659	0.7439
In which of these groups did your total household income for last year fall?[5-4]	0.141498	0.9339

In which of these groups did your total household income for last year fall?[6-5]	-0.21761	0.8839
How long have you been living in Torch Lake Township?	0.013761	0.5222
Whom did you vote in the last Presidential elections?[1]	0.801983	0.3822
Whom did you vote in the last Presidential elections?[2]	0.422379	0.4977
Whom did you vote in the last Presidential elections?[3]	-0.19301	0.7728
Whom did you vote in the last Presidential elections?[4]	-0.99823	0.4398
Do you consider yourself religious?[1]	0.066419	0.8818

### 4.3 Conclusions

The door to door survey was achieved with a response rate of 68.1% and every effort was made to get a representational sample of the Torch Lake Township, Upper Peninsula of MI. Fifty eight percent of the respondents were male and forty two percent of the respondents were female. Almost all (99%) of the respondents identified their race as white and 80% respondents considered themselves as religious. More than half of respondents (56%) had a college degree and annual household income of 41% respondents was more than \$45,000. College education (BA/BS) and annual household income (\$30,000-44,999) were significantly correlated with global environmental issue of climate change. The respondents overwhelmingly supported our research project to be started in their community as they were concerned with stamp sand erosion into the Torch Lake. They were also aware of global environmental issues like climate change and acknowledged that climate change is real and we need to protect our planet from climate change. However, they agreed equally to the cause of climate change whether it is natural occurring or caused by anthropogenic activities.

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## Appendix A      A 1: Approval letter for the research study (survey) from IRB

 **MONTCLAIR STATE  
UNIVERSITY**

Institutional Review Board  
College Hall, Room 248  
VOICE: 973-655-7583  
FAX: 973-655-3022

June 10, 2014

Mr. Virinder Sidhu  
209 Davey Street, Apt. A  
Bloomfield, NJ 07003

Re: IRB Number: **001526**  
Project Title: **Establishing a Vegetative Cap for Sustainable Stabilization of Copper Contaminated Soils in Torch Lake, Michigan**

Dear Mr. Sidhu:

After an expedited 7 review, Montclair State University's Institutional Review Board (IRB) approved this protocol on **May 8, 2014**. The study is valid for one year and will expire on **May 8, 2015**.

Before requesting amendments, extensions, or project closure, please reference MSU's IRB website and download the current forms.

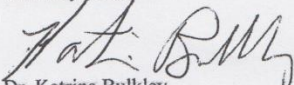
Should you wish to make changes to the IRB-approved procedures, prior to the expiration of your approval, submit your requests using the Amendment form.

For Continuing Review, it is advised that you submit your form 60 days before the month of the expiration date above. If you have not received MSU's IRB approval by your study's expiration date, **ALL** research activities must STOP, including data analysis. If your research continues without MSU's IRB approval, you will be in violation of Federal and other regulations.

**Please note, as the principal investigator, you are required to maintain a file of approved human subject's research documents, for each IRB application, to comply with federal and institutional policies on record retention.**

After your study is completed, submit your Project Completion form.


If you have any questions regarding the IRB requirements, please contact me at 973-655-5189, [reviewboard@mail.montclair.edu](mailto:reviewboard@mail.montclair.edu), or the Institutional Review Board.

Sincerely yours,  
  
Dr. Katrina Bulkley  
IRB Chair

cc: Dr. Yong Wang, Faculty Sponsor  
Ms. Amy Aiello, Graduate School

montclair.edu  
1 Normal Avenue • Montclair, NJ 07043 • An Equal Opportunity/Affirmative Action Institution

## A 2: Approval letter for amendment to the research study (survey) from IRB

 **MONTCLAIR STATE**  
UNIVERSITY

Institutional Review Board  
College Hall, Room 248  
VOICE: 973-655-7583  
FAX: 973-655-3022

July 16, 2014

Mr. Virinder Sidhu  
209 Davey Street, Apt. A  
Bloomfield, NJ 07003

Re: IRB Number: **001526**  
Project Title: **Establishing a Vegetative Cap for Sustainable Stabilization of Copper Contaminated Soils in Torch Lake, Michigan**

Dear Mr. Sidhu:

After an expedited 4 review, Montclair State University's Institutional Review Board (IRB) approved this study's amendment on **July 15, 2014** (submitted on July 3, 2014). It is valid through the current approved period and will expire on **May 8, 2015**.

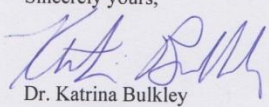
Before requesting amendments, extensions, or project closure, please reference MSU's IRB website and download the current forms.

Should you wish to make changes to the IRB-approved procedures, prior to the expiration of your approval, submit your requests using the Amendment form.

For Continuing Review, it is advised that you submit your form 60 days before the month of the expiration date above. If you have not received MSU's IRB approval by your study's expiration date, ALL research activities must STOP, including data analysis. If your research continues without MSU's IRB approval, you will be in violation of Federal and other regulations.

After your study is completed, submit your Project Completion form.

If you have any questions regarding the IRB requirements, please contact me at 973-655-5189, [reviewboard@mail.montclair.edu](mailto:reviewboard@mail.montclair.edu), or the Institutional Review Board.


Sincerely yours,  
  
Dr. Katrina Bulkley  
IRB Chair

cc: Dr. Yong Wang, Faculty Sponsor  
Ms. Amy Aiello, Graduate School

[montclair.edu](http://montclair.edu)  
1 Normal Avenue • Montclair, NJ 07043 • An Equal Opportunity/Affirmative Action Institution



## A 3: Approval letter for continuing review of the research study (survey) from IRB

 **MONTCLAIR STATE**  
UNIVERSITY

Institutional Review Board  
College Hall, Room 248  
VOICE: 973-655-7583  
FAX: 973-655-3022

March 23, 2015

Mr. Virinder Sidhu  
209 Davey Street, Apt. A  
Bloomfield, NJ 07003

Re: IRB Number: **001526**  
Project Title: **Establishing a Vegetative Cap for Sustainable Stabilization of Copper Contaminated Soils in Torch Lake, Michigan**

Dear Mr. Sidhu:

After an expedited 7 review, Montclair State University's Institutional Review Board (IRB) approved your Continuing Review request on **March 20, 2015**. The continuation is valid for one year and will expire on **May 8, 2016**.

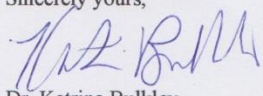
Before requesting amendments, extensions, or project closure, please reference MSU's IRB website and download the current forms.

Should you wish to make changes to the IRB-approved procedures, prior to the expiration of your approval, submit your requests using the Amendment form.

For Continuing Review, it is advised that you submit your form 60 days before the month of the expiration date above. If you have not received MSU's IRB approval by your study's expiration date, ALL research activities must STOP, including data analysis. If your research continues without MSU's IRB approval, you will be in violation of Federal and other regulations.

After your study is completed, submit your Project Completion form.

If you have any questions regarding the IRB requirements, please contact me at 973-655-5189, [reviewboard@mail.montclair.edu](mailto:reviewboard@mail.montclair.edu), or the Institutional Review Board.

Sincerely yours,  
  
Dr. Katrina Bulkley  
IRB Chair

cc: Dr. Yong Wang, Faculty Sponsor  
Ms. Amy Aiello, Graduate School

[montclair.edu](http://montclair.edu)  
1 Normal Avenue • Montclair, NJ 07043 • An Equal Opportunity/Affirmative Action Institution

## Appendix B 1: Letter of agreement (first) from Torch Lake Township for the survey

Brian Cadwell, Supervisor  
Karen Rovano, Clerk  
Diane Zurcher, Treasurer  
Brian Foreman, Trustee  
Scott Sapino, Trustee



52235 Duncan Avenue  
P.O. Box 429  
Hubbell, MI 49934  
Phone: (906) 296-0214  
Fax: (906) 296-9540

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May 29, 2014

Attn: Institutional Review Board  
Montclair State University  
1 Normal Avenue  
College Hall, Room 248  
Montclair, NJ 07043

Re: [Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan. PI: Virinder Sidhu]

Dear Review Board,

This letter serves to give permission to Virinder Sidhu to complete his research project, "Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan" during time frame, i.e. September/October 2014 at our facility.

Virinder Sidhu will have access to our residents to conduct his research project. The research project has been described to me to my satisfaction.

Please do not hesitate to call if I you have any questions or I may be of further assistance.

Sincerely,

*Brian Cadwell*

Brian Cadwell  
Supervisor  
Torch Lake Township  
Cell: 906-370-5097

## B 2: Letter of agreement (second) from Torch Lake Township for the survey

Brian Cadwell, Supervisor  
Karen Rovano, Clerk  
Diane Zurcher, Treasurer  
Brian Foreman, Trustee  
Scott Sapino, Trustee



S2235 Duncan Avenue  
P. O. Box 429  
Hubbell, MI 49934  
Phone: (906) 296-0214  
Fax: (906) 296-9540

March 16, 2015

Attn: Institutional Review Board  
Montclair State University  
1 Normal Avenue  
College Hall, Room 248  
Montclair, NJ 07043


Re: [Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan. PI: Virinder Sidhu]

Dear Review Board,

This letter serves to give permission to Virinder Sidhu to complete his research project, "Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan" during time frame, i.e. May, June, July and August 2015 at our facility.

Virinder Sidhu will have access to our residents to conduct his research project. The research project has been described to me to my satisfaction.

Sincerely,

  
Brian Cadwell, Township Supervisor



## Appendix C: Pre-notification letter for the survey

**Pre-notification Letter for Survey**

Dear Torch Lake Township residents,

We will be doing a survey of your community of Torch Lake Township in June-July, 2015 about starting our project, "Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan". We will go door to door for the survey. The participants will fill out a survey questionnaire given by us. In one household, not more than one adult will fill out the survey questionnaire. It will take about 10-15 minutes to fill in the survey questionnaire.

Your responses will help us in designing a better research project for Torch Lake. Others may benefit from this study because this study will help find new ways for growing crops on marginal lands. These crops will prevent soil erosion and also provide a source of bio fuel. Torch Lake can serve as a model for this solution.

Your participation in the survey will be voluntary. Your identity will be kept confidential. Thank you for your time and anticipating cooperation during the survey.

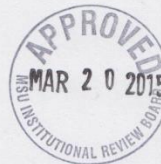
Sincerely,

Project Investigator (PI):

Virinder Sidhu  
Ph.D. Candidate (Environmental Management)  
Department of Earth and Environmental Studies  
358N, Mallory Hall  
Montclair State University  
NJ 07043  
973-655-3456  
sidhuv1@mail.montclair.edu

Faculty Sponsor of PI:

Dr Yong Wang  
Associate Professor  
Department of Sociology  
311, Dickson Hall  
Montclair State University  
NJ 07043  
973-655-7071  
wangy@mail.montclair.edu



## Appendix D: Consent form for adults for the survey (page 1)



**MONTCLAIR STATE**  
UNIVERSITY

*College of Science and Mathematics*

Department of Earth and Environmental Studies

Voice: 973-655-3456

Fax: 973-655-4072

### CONSENT FORM FOR ADULTS

Please read below with care. You can ask questions at any time, now or later. You can talk to other people before you sign this form.

**Study's Title:**

Establishing a vegetative cap for sustainable stabilization of copper contaminated soils in Torch Lake, Michigan.

**Why is this study being done?**

Large scale mining activities occurred during the late 19<sup>th</sup> to early 20<sup>th</sup> century in this region of Michigan. That mining has resulted in several contaminated sites. Several million tons of residues were formed due to mining. Those residues are called "stamp sands". Stamp sands were made by crushing rocks with copper in them. These stamp sands eroded into Lake Superior, and other lakes. The copper polluted sands are being eroded back into the lakes. This affects the lake bottom community.

We are conducting a research study to grow native oil seed crops. Oil seed crops such as "camelina" and "field pennycress" will reduce soil erosion. The seeds from these crops will also serve as a source of bio fuel. This study will help find new ways for growing these crops on marginal lands. These crops will prevent soil erosion and also provide a source of bio fuel. Torch Lake can serve as a model for this solution.

We are doing a survey of your community of Torch Lake Township. We hope to gauge the views of the local residents about starting our project here.

**What will happen while you are in the study?**

I will go door to door for administering the survey questionnaire. The participants will fill out a survey questionnaire given by me. In one household, not more than one adult will fill out the survey questionnaire.

**Time:**

It will take 10-15 minutes to fill in the survey.

**Risks:**

The risks are no greater than those in ordinary life.

We will keep your identity confidential as it relates to this research project. But, if we learn of any suspected child abuse. Then, we are required by NJ state law to report that to the proper authorities immediately.

**Benefits:**

Your responses will help us in designing a better research project for Torch Lake. We also hope to gauge the views of the local residents about environment.

Others may benefit from this study because this study will help find new ways for growing crops on marginal lands. These crops will prevent soil erosion and also provide a source of bio fuel. Torch Lake can serve as a model for this solution.





Appendix D: Consent form for adults for the survey (page 2)



**MONTCLAIR STATE UNIVERSITY**

*College of Science and Mathematics*  
 Department of Earth and Environmental Studies  
 Voice: 973-655-3456  
 Fax: 973-655-4072

**Who will know that you are in this study?**

You will not be linked to any presentations. We will keep who you are as confidential.

**Do you have to be in the study?**

You do not have to be in this study. You are a volunteer! It is okay if you want to stop at any time and not be in the study. You do not have to answer any questions you do not want to answer. Nothing will happen to you.

**Do you have any questions about this study?**

Phone or email the Principal Investigator:

Virinder Sidhu  
 Ph.D. Candidate (Environmental Management)  
 Department of Earth and Environmental Studies  
 358N, Mallory Hall  
 Montclair State University  
 Montclair, NJ 07043  
 Phone: 973-655-3456  
 sidhuv1@mail.montclair.edu

Principal Investigator's Faculty Sponsor:

Dr Yong Wang  
 Associate Professor  
 Department of Sociology  
 311, Dickson Hall  
 Montclair State University  
 Montclair, NJ 07043  
 Phone: 973-655-7170  
 wangy@mail.montclair.edu

**Do you have any questions about your rights as a research participant?** Phone or email the IRB Chair, Dr. Katrina Bulkley, at 973-655-5189 or [reviewboard@mail.montclair.edu](mailto:reviewboard@mail.montclair.edu).

**One copy of this consent form is for you to keep.**

**Statement of Consent**

I have read this form and decided that I will participate in the project described above. Its general purposes, the particulars of involvement, and possible risks and inconveniences have been explained to my satisfaction. I understand that I can withdraw at any time. My signature also indicates that I am 18 years of age or older and have received a copy of this consent form.

_____	_____	_____
Print your name here	Sign your name here	Date
Virinder Sidhu	_____	_____
Name of Principal Investigator	Signature	Date
Dr. Yang Wong	_____	_____
Name of Faculty Sponsor	Signature	Date



## Appendix E: Survey questionnaire for the research study (page 1)

**Survey Questionnaire on Torch Lake Soils**

Do you agree or disagree with the following statements?

1. I value the environment.
  - Yes
  - No
2. I know about high levels of copper in Torch Lake.
  - Yes
  - No
3. I know about high levels of copper in the soil around Torch Lake.
  - Yes
  - No
4. Erosion of soil with high copper levels is a concern on the banks of Torch Lake.
  - Yes
  - No

How much do you agree or disagree with the following statements?

5. High copper levels in Torch Lake and its surrounding area concerns you.
  - Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
6. A scientific project to reduce erosion of soil with high copper levels into Torch Lake would be supported by you.
  - Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree



## Appendix E: Survey questionnaire for the research study (page 2)

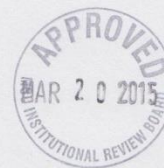
7. The reduction of erosion of soil with high copper levels into Torch Lake will be beneficial for water quality.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
8. The project includes two native oilseed crops (“Camelina” and “Field Pennycress”), which can be used to make biodiesel in addition to reducing erosion of soil into Torch Lake with high copper levels. I would approve of such a project if asked.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
9. The revenue earned from the sale of oilseeds of Camelina and Field Pennycress will benefit your community and the oilseeds can be used to produce biodiesel.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree*
10. This project can lead to the creation of jobs in your community.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
11. This project can lead to the greater use of Torch Lake as a recreational area.
- Strongly agree
  - Somewhat agree
  - Agree



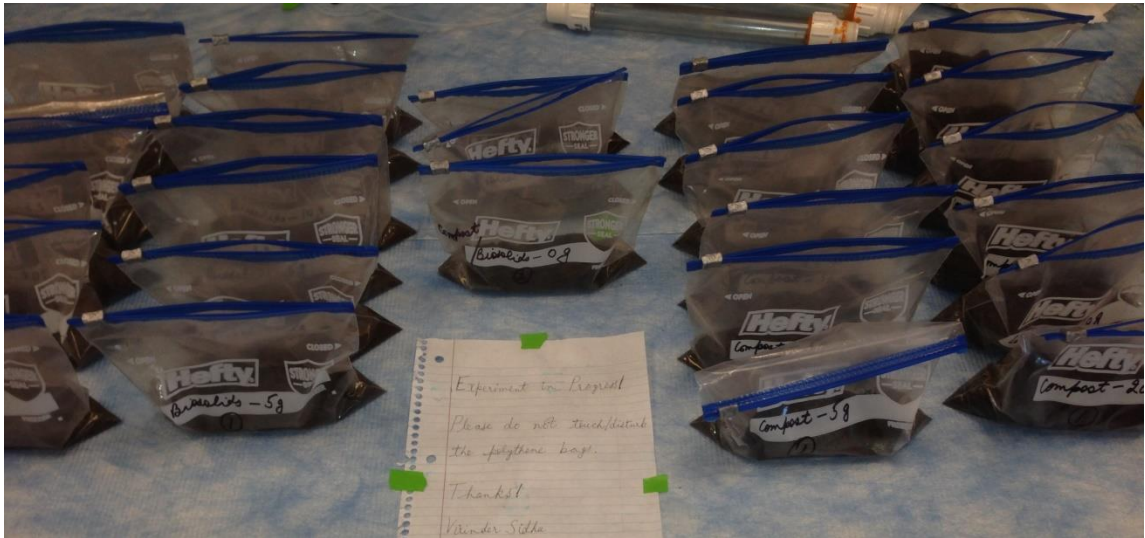


## Appendix E: Survey questionnaire for the research study (page 3)

- Somewhat disagree
  - Disagree
  - Strongly disagree
12. Which of the following institutions should undertake such a project in your township?
- Federal agency (US EPA)
  - State agency (MDEQ)
  - Local government (Torch Lake Township)
  - Private company
  - Public-Private partnership
  - None of the above
13. Climate change is real.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
14. Climate change is caused by the activities of people.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
15. Climate change is a natural occurring process.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree
  - Disagree
  - Strongly disagree
16. We need to protect our planet from climate change.
- Strongly agree
  - Somewhat agree
  - Agree
  - Somewhat disagree



## Appendix F



F 1: Picture of the incubation study in the laboratory in progress.



F 2: Picture of the greenhouse column study with camelina (*Camelina sativa*) in progress.





F 3: Picture of the greenhouse column study with field pennycress (*Thlaspi arvense*) in progress.



F 4: Picture of the field simulation study with camelina (*Camelina sativa*) and control (no plant) in the wooden panels in greenhouse in progress.

