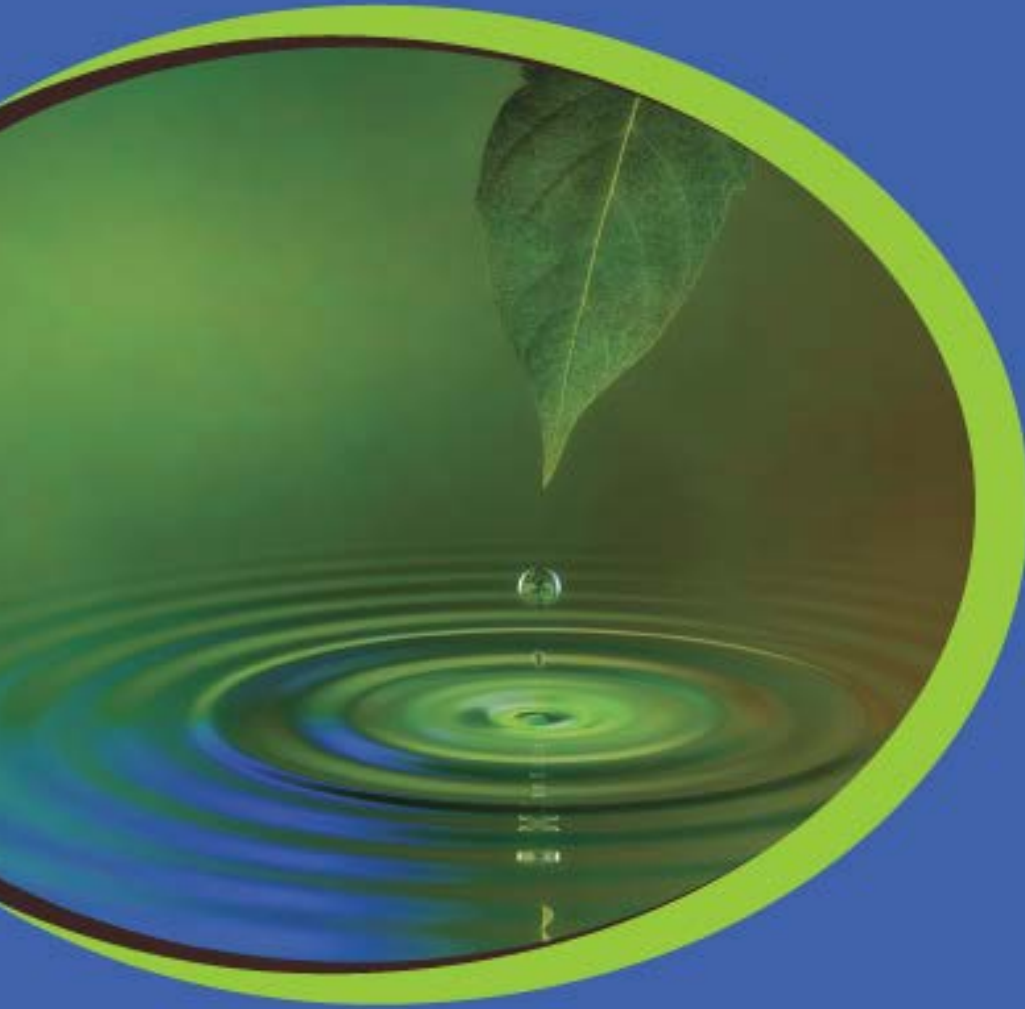


# REPORT

## IS RESIDENTIAL WOOD ASH SAFE FOR USE TO HELP SOLVE THE CALCIUM DECLINE PROBLEM IN MUSKOKA?



Shakira Azan, PhD



Friends of the  
Muskoka  
Watershed

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**Report # 2018-01-HATSEO-2**

Please direct all questions and comments to:

[friends@fotmw.org](mailto:friends@fotmw.org)

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# List of Abbreviations

Ca - Calcium ( $\text{Ca}^{2+}$ )

$\text{CaCO}_3$  – Calcium carbonate

$\text{CO}_2$  – Carbon dioxide

DESC - Dorset Environmental Science Centre

DF – Dilution factor

DW - Dry weight

FLAMES – Field Laboratory for the Assessment of Multiple Ecological Stressors

FMW – Friends of the Muskoka Watershed

HATSEO – Hauling Ash to Solve Ecological Osteoporosis

LOI – Loss on ignition

MOECC - Ministry of the Environment and Climate Change

$\text{K}_2\text{CO}_3$  – Potassium carbonate

KCL – Potassium chloride

TP - Total phosphorus

# **Chapter 1**

## **General Introduction**

## **CALCIUM DECLINE**

Levels of calcium (Ca), a critical mineral for the health of plants (terrestrial and aquatic) and animals have declined in Canadian Shield lakes in eastern North America. Ca is important for shell building and carapace strengthening in molluscs (e.g., snails and crayfish), holding plant cells together in trees, and maintaining healthy bones and teeth, nerve impulses, and muscle contractions in mammals, i.e., you and me. Several decades of acid deposition have leached mobile Ca from catchment soil pools. The loss of Ca from soil pools has been exacerbated by repeated cycles of logging and/or land clearing and re-growth of forests. Soil weathering, the process that replenishes Ca in the soil, is a very slow process. Thus, as the rate of export of Ca from the soil pools exceeds the rate of input through weathering, atmospheric dust and precipitation, Ca levels in the soil have declined. Lakes get their Ca mainly from the soils of surrounding watersheds. Therefore, as Ca levels in watershed soils decline, so do the Ca concentrations in the lakes. And somewhat ironically, recent reductions in acid deposition have hastened the decline, as the residual soil Ca pools are now being leached at a slower rate.

The impacts from the loss of Ca have been particularly severe in Muskoka where watersheds have thin soils with low capacity to buffer acid deposition as they lie on Ca-poor bedrock. The loss of Ca is disrupting the ecology of both the forests and lakes of Muskoka. In forests, low Ca levels have resulted in slowed growth and seedling production, reduced regeneration and dieback of sugar maple - a Ca rich tree species<sup>1</sup> - that might impact maple syrup production. In lakes, crayfish with their high Ca demands are disappearing (Edwards et al. 2009). Currently, the fate of other nearshore crustaceans and molluscs, all Ca-rich

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<sup>1</sup> Sugar maple leaves contain about 1.8% calcium

groups of species is unknown, but they are likely to be impacted by the loss of Ca. Last, in offshore waters, a jelly-clad water flea, *Holopedium*, is replacing its more Ca-rich competitor, *Daphnia*. Loss of several Ca-rich animal plankton in our lakes increases the risk of algal blooms that can impair and reduce water quality. Increased abundances of *Holopedium* also increases the likelihood of clogged water filters for residents drawing their water from lakes.

## **HOW CAN WE COMBAT CALCIUM DECLINE?**

One possible solution to combatting Ca decline is to supplement soil Ca with a natural and available additive, such as wood ash. Wood ash – the residue obtained from the combustion of wood – is generated by residents of the Muskoka during the heating season. Through active local engagement, Muskokans can become “gardeners of the forest” by returning an easily accessible waste product – wood ash - to the forest from which it originated. Wood ash contains many elements – both major and minor – that are required for tree growth. Of the elements present, Ca is the most abundant, along with potassium (K), magnesium (Mg), and phosphorus (P) (Reid and Watmough 2014), while levels of nitrogen (N) are low (Hannam et al. 2016). The amount of Ca in wood ash depends on the tree species burned, the presence of tree bark, which has high Ca levels, and the chemistry of the soil supporting the fuel wood (Reid and Watmough 2014). These drivers produce Ca levels in wood ash that vary from 15% (Risse and Gaskin 2002) to 50% (Perry, n.d.) of total ash weight.

Wood ash is commonly used as a forest or soil amendment elsewhere. In Sweden, Finland, and the United Kingdom, wood ash is frequently added to forest soils to enhance biomass production. In some cases, wood ash has been used to increase soil pH, soil fertility and productivity, and as a means of returning and/or recycling nutrients back to the forest

(Hannam et al. 2016). In Canada, the use of wood ash as a soil amendment is regulated by each province or territory and as such, varies across Canada. It is mainly used for liming and/or fertilizing in Alberta, British Columbia, New Brunswick, Nova Scotia, and Quebec. In Ontario, wood ash is not frequently used as a soil amendment for agricultural or forest soils and there are currently no specific guidelines for such uses (Hannam et al. 2016). We think this is a lost opportunity.

## **HATSEO AND WOOD ASH**

Under the 'Hauling Ash to Solve Ecological Osteoporosis' or 'HATSEO' project, the Friends of the Muskoka Watershed (FMW) is investigating the feasibility of using residential wood ash as a soil amendment in Muskoka to help combat Ca decline in our forest soils, and indirectly our lakes. By applying residential wood ash to forest soils, we are converting a waste product into a useful forest fertilizer. Addition of wood ash that contains about 15-50% of Ca might increase soil Ca pools, and subsequent soil leaching could increase Ca levels in our lakes. Through applied research, the FMW will quantify the nutrient and metal chemistry and solubility of residential wood ash, and its potential toxicity to *Daphnia*, a key herbivore in freshwater lakes. Just as white rats are used in laboratories to test the toxicity of substances in the food supply, *Daphnia* are an organism of choice for testing the toxicity of chemicals or substances that might enter aquatic ecosystems. As such, they are referred to as the "white rat" of aquatic toxicology. Our research findings seek to satisfy the regulatory requirements prior to the development and testing of a large-scale wood ash recycling programme designed to help alleviate the Ca decline problem in our forests and lakes.

## REPORT OBJECTIVES

The overarching goal of the HATSEO project is to evaluate the use of residential wood ash - a readily available waste product - to help solve the Ca decline problem in Muskoka forests and lakes. In Chapter 1 of this report, the metal concentrations of 11 regulated trace metals in 14 local sources of residential wood ash are reported. The concentrations of the trace metals are then compared with target thresholds of the content of regulated materials (CM) for non-aqueous non-agricultural source materials (NASM) set by Ontario Regulations 267/03 of the *Nutrient Management Act* (Government of Ontario 2002). This analysis revealed that the metal concentration in the vast majority of the wood ash samples fell well below the CM1 level with two exceptions. Levels of the essential metals, copper and zinc, slightly exceeded CM1 (the level set for unrestricted use), but were well below CM2 levels. Wood ash with metal concentration above CM2 guidelines are treated as hazardous waste that must be landfilled. None of our ash samples had any metal levels that approached or exceeded CM2 guidelines. The amount of carbonates in the dry ash are also examined in Chapter 1. This component provides information on the amount of carbonate that is present in wood ash samples, particularly on the mineral form of the Ca, an important feature for explaining its aqueous solubility.

Chapter 2 of this report addresses the water solubility of wood ash samples over 30 days. This experiment revealed that wood ash types varied in readily extractable nutrients, with ash from wood pellet combustion exhibiting a higher percentage of Ca compared to hardwood and hardwood-softwood mix of ash. The results indicated that following land application, wood ash would likely slowly release nutrients (e.g., Ca, potassium, and phosphorus) over time to the environment.

Chapter 3 of this report addresses the short-term aquatic toxicity and longer term sediment toxicity of wood ash on *Daphnia*, the common water flea that is the “white rat” of aquatic toxicology. These experiments revealed some toxicity of wood ash elutriate concentrates on *Daphnia* in the short-term. This was not a surprise given that the Concentrate was the product of a 10% ash solution, i.e., 1 part ash in 9 parts of water. The short-term toxicity was not attributable to metals or high pH, as we first suspected, but to high levels of soluble potassium, a nutrient, in our concentrates. As this potassium is rapidly diluted in nature, we consider this observation of toxicity in our concentrates to be a simple product of our use of high sediment to water ratios in our undiluted bioassays. We do not believe it is of much environmental relevance.

## **Chapter 2**

### **Metal and carbonate levels in residential wood ash**



## **ABSTRACT**

Wood ash can supply important nutrients for plant and animal growth and development. However, it also contains heavy metals that can be harmful to aquatic environments. We measured levels of 11 trace metals of concern to the Government of Canada in 14 local dry wood ash samples collected from Muskoka residents. With the exception of copper and zinc that fell just above CM1, but well below CM2 levels, the remaining nine metals fell well below CM1 guidelines, suggesting that local residential wood ash should normally be usable as a soil amendment. Although wood pellet ash contained the highest percentage of calcium (Ca), all three wood ash types have enough Ca that we believe they could be used as a forest soil additive to help solve the “ecological osteoporosis” problem in Muskoka forests and lakes.

## **INTRODUCTION**

Metals are common pollutants of freshwater environments the world over. Many of them are soluble in water and can be easily adsorbed onto the gills of aquatic animals such as insect larvae, water fleas, and fish, such adsorption being the first step in a toxic effect. Metals are found everywhere in the environment, including in trees, and thus in wood ash, but their levels may vary. Irrespective of province or territory, the Government of Canada requires wood ash to be analysed for 11 trace metals (arsenic, cadmium, chromium, cobalt, copper, mercury, molybdenum, nickel, lead, selenium and zinc) prior to consideration for approval as a soil amendment. Wood ash that exceeds the upper guideline for content of any of the regulated metal (CM) levels must be treated and disposed of as hazardous waste (Hannam et al. 2016). There are two CM levels: CM1 and CM2 (Table 2.1). If metal levels in the wood ash are below CM1 targets, they may be considered for unrestricted application. Where

metal levels in the wood ash fall between CM1 and CM2, they may be used depending on the background metal levels in the soil. If metal levels in the wood ash exceed the CM2 target, the ash may not be used as a soil additive. The application of wood ash with metal levels above CM2 to watershed soils is assumed to produce a leachate<sup>2</sup> with metal levels that could result in metal toxicity to organisms.

Metal toxicity can produce adverse effects on an organism's survival, growth, metabolism or reproduction (Solomon 2008). For example, high mercury levels can result in the reduction of hatching rates and growth and development for fish, and birds. In humans, for example, decades of consumption of fish and shellfish exposed to high levels of mercury has resulted in a neurological condition called Minamata disease. The severity of metal toxicity is site-specific, influenced by metal concentration, water pH, redox potential, and organic carbon content, which influence metal speciation<sup>3</sup>, and Ca concentration, as Ca competes with metals for uptake sites on biological membranes.

Despite the plethora of knowledge on the likely impacts of metal toxicity (e.g., Förstner and Whitman 1981), no field or laboratory research has been conducted to evaluate the metal levels in residential wood ash or the toxicity of wood ash in aquatic media. Here, we present the results of laboratory determinations of metal levels in residential wood ash as well as the amount of carbonates present. This knowledge is important given the Government of Canada's requirements for metal assays as a component of the evaluation of the potential use of wood ash as a soil amendment.

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<sup>2</sup> Leachate is water that has percolated through a column of soil and leached out some of its constituents (Oxford Dictionary)

<sup>3</sup> Metal speciation refers to the different chemical forms that a metal can exist, e.g., as free metal ions, carbonates, hydroxides, etc.

## **MATERIALS AND METHODS**

### ***Main sources of wood***

Several types of wood are used during the heating season in Muskoka. From the *Survey of Wood Ash Users in Muskoka* (Azan 2017), we confirmed common knowledge, i.e., that residents mainly used hardwood tree species (57% of respondents) such as maple, beech, oak, birch, ash, and cherry. Some residents also used softwood tree species such as hemlock, pine, spruce, and cedar (14% of respondents) and wood pellet (3% of respondents). Based on these results, we divided wood ash samples collected from 14 local residents into these types: hardwood, wood pellet, and hardwood-softwood mix. The last type represents those residents that burn hardwood and softwood tree species either in a stove or in campfires and mix the ash prior to making it available to us.

### ***Metal analysis***

To assess the concentration of the 11 trace metals in wood ash, we collected samples from 14 local residents located in Baysville, Bracebridge, and Port Carling, Ontario. Samples were initially sieved using a stainless steel riddle<sup>4</sup> with a mesh size of 3/32" to remove occasional foreign objects including nails and staples, and the coarse clinker that is normally generated by incomplete wood combustion. Prior to analysis, 30 g of wood ash was weighed from each ash sample, re-sieved using a Nitex 355 µm mesh and then divided into three equal parts for analysis. In total, 42 dry ash samples (n=30 for hardwood; n=9 for hardwood-softwood mix; n=3 for wood pellet) were analysed by the Ministry of the Environment and Climate Change

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<sup>4</sup> A large coarse sieve, especially one used for separating ashes from cinders or sand from gravel (Oxford Dictionary)

(MOECC), Laboratory Services Branch located in Toronto, Ontario using: 1) cold vapour atomic absorption spectrophotometry (AAS) for mercury; 2) hydride-flameless AAS for arsenic, selenium, and antimony; and 3) hot block digestion and inductively coupled plasma – optical emission spectrophotometry for all other metals (e.g., Ca, magnesium, and potassium).

### ***Loss on ignition***

We used Dean's (1974) loss on ignition (LOI) method to determine the carbonate and organic matter present in the 14 wood ash samples collected. The method is briefly described here. In a pre-weighed ceramic crucible, 1 g of wood ash was dried using a conventional oven (Despatch Industries, model# LEB1-27) for 1 hour at 125°C. After cooling, the sample and crucible were weighed. This recorded value was the dry weight ( $w_1$ ) of the sample. The sample and crucible were then heated in a muffle furnace (Barnstead International type 48000, model #F48015) at 500°C for 1 hour. After cooling, the sample and crucible were re-weighed ( $w_2$ ). Sample and crucible were returned to the furnace and heated at 1000°C for 1 hour. Following cooling, the sample and crucible were weighed ( $w_3$ ). The difference between ( $w_1$ ) and ( $w_2$ ) was the amount of organic matter ignited whereas the difference between ( $w_1$ ) and ( $w_3$ ) was the amount of carbon dioxide ( $\text{CO}_2$ ) evolved from carbonate minerals in the ash sample.

## RESULTS

### Trace metal concentrations

The majority of all the metal concentrations in the three wood ash types analysed fell below the CM1 standard. The exceptions were copper and zinc with mean concentrations just above the CM1 target, but still well below the CM2 level for some wood ash types (Table 2.2). All 30 individual hardwood samples analysed fell below the CM1 standard for arsenic, chromium, cobalt, lead, mercury, nickel, and selenium, while 7 of the cadmium and 9 of the individual molybdenum samples somewhat exceeded the CM1 standard. Mean levels of these metals were below CM1. In hardwood-softwood mix samples, only 3 samples fell above the CM1 level for cadmium. Like hardwood, all wood pellet samples were equivalent to the CM1 level for molybdenum.

Metal levels were above the CM1 target but below CM2 levels in 13 of 30 hardwood and 6 of 9 hardwood-softwood mix samples for copper, and 18 of 30 hardwood and 5 of 9 hardwood-softwood mix samples for zinc. However, the hardwood samples were, on average, ~174% and 97%<sup>5</sup> lower than the CM2 level for copper and zinc, respectively. Similarly, hardwood-softwood mix samples were, on average, ~164% and 148% lower than the CM2 level for copper and zinc, respectively. In all wood pellet samples, concentrations fell above the CM1 level, but were, on average, ~173% and ~146% lower than the CM2 target for copper and zinc, respectively. Two hardwood-softwood mix ash samples were equivalent to the CM1 level for both copper and zinc. None of our samples fell above the CM2 targets listed for the 11 trace metals.

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<sup>5</sup> These calculations and others found throughout the report were done using "Percentage difference", i.e., the difference between two positive numbers that are greater than zero.

### Nutrient concentrations

In general, nutrient concentrations varied with ash type. We discovered that wood pellet ash was comprised, on average, of 37% Ca compared to hardwood and hardwood-softwood mix of ash that contained relatively lower levels of Ca (mean 29% to 30%) (Figure 2.1). We also found that both hardwood and hardwood-softwood mix of ash contained similar levels of potassium, of about 8%. In contrast, wood pellet contained slightly lower levels of potassium with a mean of 6% (Figure 2.2). We also detected similar levels of magnesium in hardwood and hardwood-softwood mix of ash. On average, these levels were 2%. In contrast, mean levels of magnesium were higher in wood pellet (~4%) (Figure 2.3). For all wood types used, phosphorus levels were relatively similar, with mean ranges between 0.7% and 0.8% (Figure 2.4).

### Loss on ignition

Overall, the level of organic matter and carbonates varied within wood ash types. Of the three ash types used, we discovered that wood pellet contained the lowest percentage of organic matter (on average ~0.5%) compared to hardwood and hardwood-softwood mix of ash. The organic matter content in these ash types were much higher than those observed for wood pellet and were, on average, between 3% and 4% (Figure 2.5).

Like organic matter content, we discovered that wood pellet released, on average, the lowest amount of carbon dioxide (CO<sub>2</sub>) at 19% compared to hardwood and hardwood-softwood mix of ash. In addition, we found that hardwood and hardwood-softwood mix of ash were relatively similar and contained between 29% and 30% of carbonate by weight (Figure 2.6).

## **DISCUSSION**

The majority of metal concentrations found in hardwood, hardwood-softwood mix, and wood pellet ash fell well below the regulated levels for CM1. For these metals, our results suggest that wood ash would not pose any toxic threat as a soil amendment in Muskoka. There is however, some concern with regards to copper and zinc, two metals with average levels that fell above the CM1, but well below the CM2 standard. Although 30 out of 39 hardwood and hardwood-softwood mix ash samples had at least one metal, normally, copper or zinc, that exceeded the CM1 target, we do not believe that the use of these ash types would result in metal toxicity in the receiving soils or waters, as copper and zinc are essential metals that plants and animals can readily sequester, and copper at least is strongly bound to organics and rendered non-toxic. In addition, our analysis was conducted on fly ash (the fine ash generated during wood burning), as all clinker was removed during sample preparation. The clinker was removed as our primary focus was on the ash component that contained the mineral phases, such as Ca, as well as to homogenize the ash sample.

Our results also suggest that wood ash application might increase Ca levels in the soil and indirectly, lake waters. We detected relatively high levels of Ca between 29% and 37% in the wood ash types we used, in agreement with Ca levels reported by Risse and Gaskin (2002) and Perry (n.d.). In order to ascertain if wood ash can increase Ca levels in the soil and indirectly, lake waters, further research is therefore required to determine how much Ca gets into soil Ca pools and groundwater following land application as well as its effect on aquatic environments.

Based on the LOI method used, we determined that wood ash contains low levels of organic matter. However, this was expected as we had removed the clinker from the ash

during sample preparation. Our wood ash samples were composed mainly of Ca compounds of which carbonate likely dominated. Although the LOI method provides an indication of how much CO<sub>2</sub> is released whilst being burnt in a muffle furnace, it does not indicate which carbonate mineral is present (e.g., CaCO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>). The method only gives information on the total carbonate content that is present in the sample. However, based on the high mean Ca levels observed in the wood ash types used, we believe that Ca carbonate (CaCO<sub>3</sub>) was probably dominant, along with some traces of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). In a study examining the composition of 5 wood ash types (hardwood and softwood) at different temperatures, Misra et al. (1993) discovered the decomposition of: 1) K<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub> at temperatures > 600°C, 2) CaCO<sub>3</sub> between 650°C and 900°C, and 3) K<sub>2</sub>CO<sub>3</sub> at temperatures > 900°C. These results support our theory that our wood ash samples likely contained both CaCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> as the Dean (1974) method required a temperature increase from 500°C to 1000°C to determine the amount of CO<sub>2</sub> evolved. However, further analysis (e.g., mass spectrometry) is required to determine specifically, which carbonate is present in the different wood ash types found in Muskoka and in what quantities.



**Table 2.1.** Standards for regulated metals in non-agricultural source materials.(Source: Schedule 5 of Ontario Regulation 267/03 of the *Nutrient Management Act* (Government of Ontario 2002))

Parameter	CM1	CM2
	Non-aqueous material (mg/kg dry weight)	Non-aqueous material (mg/kg dry weight)
Arsenic	13	170
Cadmium	3	34
Cobalt	34	340
Chromium	210	2800
Copper	100	1700
Lead	150	1100
Mercury	0.8	11
Molybdenum	5	94
Nickel	62	420
Selenium	2	34
Zinc	500	4200

**Note:** Non-agricultural source materials (NASM) that fall below CM1 levels may be considered for unrestricted use. NASM that fall between CM1 and CM2 may be used depending on the background metal levels in the soil. Other factors may be considered such as minimum depth to ground water and proximity to surface water. NASM that fall above CM2 levels cannot be applied to the land.

**Table 2.2.** Average metal concentrations (mg/kg dry weight) in ash compared to standards for unrestricted use (CM1) and restricted use (CM2).

<b>Parameter</b>	<b>Ash type</b>	<b>Ash concentration</b>	<b>CM1</b>	<b>CM2</b>
Arsenic	Hardwood	0.59	13	170
	Hardwood-softwood	1.11		
	Wood pellet	0.43		
Cadmium	Hardwood	1.91	3	34
	Hardwood-softwood	1.83		
	Wood pellet	1.43		
Chromium	Hardwood	2.89	210	2800
	Hardwood-softwood	7.48		
	Wood pellet	38.13		
Cobalt	Hardwood	1.12	34	340
	Hardwood-softwood	1.69		
	Wood pellet	2.90		
Copper	Hardwood	100.30*	100	1700

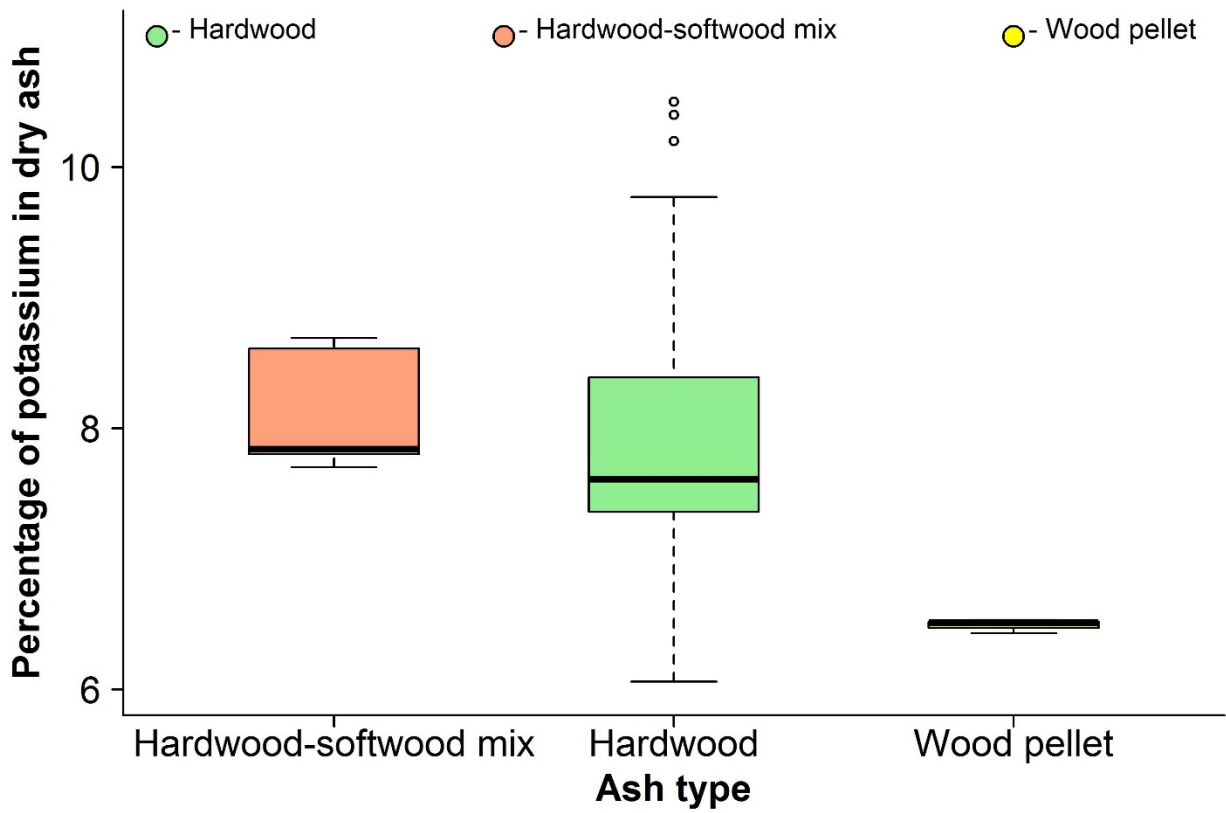
<b>Parameter</b>	<b>Ash type</b>	<b>Ash concentration</b>	<b>CM1</b>	<b>CM2</b>
	Hardwood-softwood	146.58*		
	Wood pellet	124*		
Lead	Hardwood	2.96	150	1100
	Hardwood-softwood	15.16		
	Wood pellet	5.0		
Mercury	Hardwood	0.01	0.8	11
	Hardwood-softwood	0.01		
	Wood pellet	0.01		
Molybdenum	Hardwood	2.57	5	94
	Hardwood-softwood	2.06		
	Wood pellet	5.0		
Nickel	Hardwood	4.13	62	420
	Hardwood-softwood	4.33		
	Wood pellet	2.13		
Selenium	Hardwood	0.20	2	34

<b>Parameter</b>	<b>Ash type</b>	<b>Ash concentration</b>	<b>CM1</b>	<b>CM2</b>
	Hardwood-softwood	0.20		
	Wood pellet	0.20		
Zinc	Hardwood	496.34	500	4200
	Hardwood-softwood	561.78*		
	Wood pellet	656.33*		

Note: Numbers marked by an asterisk (\*) indicate metal concentrations that fell above CM1 but below CM2 targets



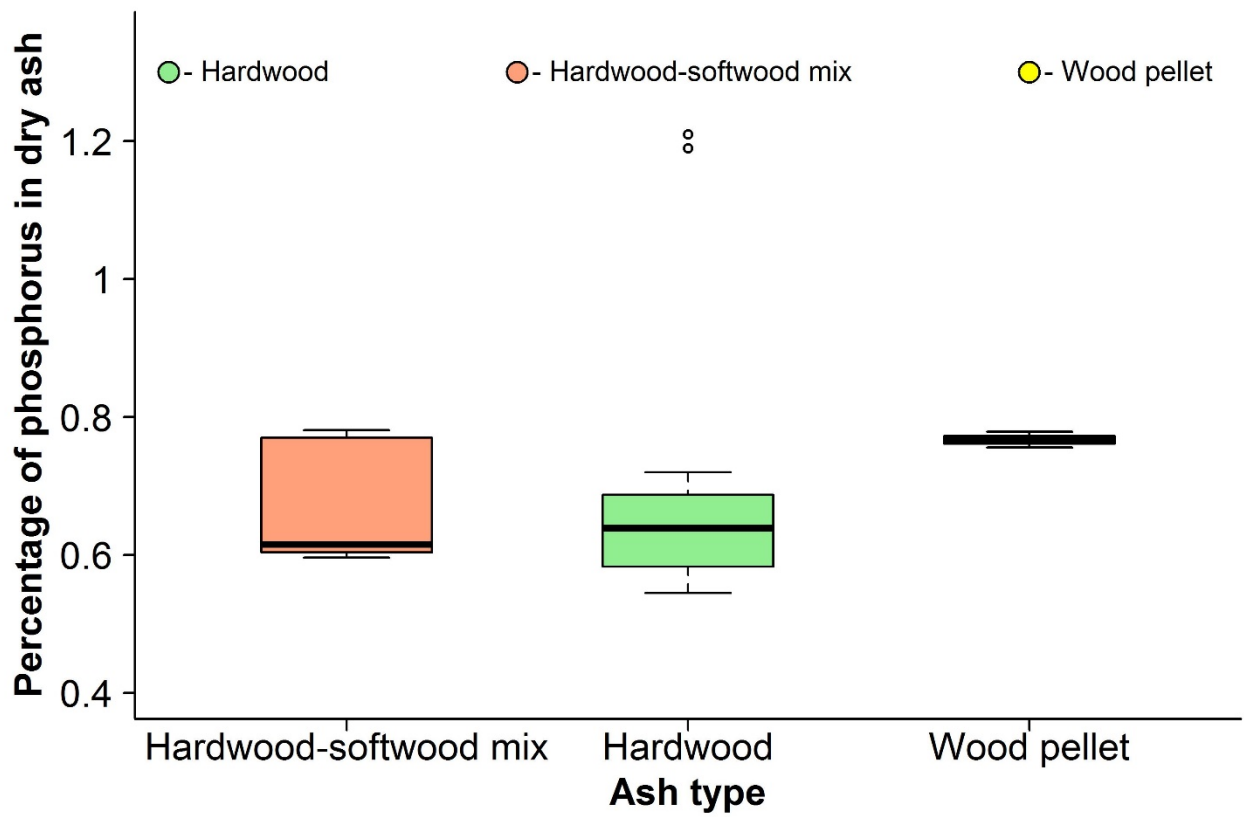
**Figure 2.1.** Box plots of calcium concentration (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



**Figure 2.2.** Box plots of potassium concentration (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



**Figure 2.3.** Box plots of magnesium concentration (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



**Figure 2.4.** Box plots of phosphorus concentration (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.





**Figure 2.5.** Box plots of organic matter (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



**Figure 2.6.** Box plots of carbonate by weight (%) in wood ash types. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.

## **Chapter 3**

### **The solubility of wood ash**

## ABSTRACT

Wood ash contains many nutrients of which calcium (Ca) is the most abundant. We conducted a 30 day laboratory experiment to determine the solubility of nutrients from three types of wood ash – hardwood, hardwood-softwood mix, and wood pellet. Wood pellet ash contained the highest amount of soluble Ca when compared to the other ash types. However, the release of Ca was much slower from the hardwood or hardwood-softwood mix of ash than from wood pellet. Hardwood-softwood mix and hardwood ash contained higher amounts of soluble potassium that was released continuously over the length of the experiment when compared to wood pellet that released potassium much more slowly over time. Our results suggest that wood ash has the potential to retain and then pulse Ca over a period of time, which would be a benefit to Muskoka forests and lakes.

## INTRODUCTION

Wood ash residue contains major and minor nutrients, all of which are essential for plant and animal growth. Ca is by far the most abundant nutrient (29% to 37%; see Chapter 2 of this report), along with potassium (~4%), phosphorus, magnesium, sodium, boron, copper, molybdenum, sulphur, and zinc (Griffin 2006). In wood ash, Ca usually exists as calcium carbonate ( $\text{CaCO}_3$ ), which is relatively alkaline and often used for liming<sup>6</sup> acid lakes and forest soils. Although  $\text{CaCO}_3$  is relatively insoluble in water (15mg/L at 25°C)<sup>7</sup>, which suggests the slow release of Ca over time, its solubility increases as temperature decreases

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<sup>6</sup> To treat soil or water with a substance that reduces acidity and improves fertility or oxygen levels (Oxford Dictionary)

<sup>7</sup> *Carbonate chemistry*. Science Learning Hub (<https://www.sciencelearn.org.nz/resources/469-carbonate-chemistry>)

and in the presence of rainwater due to the formation of the more soluble, calcium bicarbonate compound ( $\text{Ca}(\text{HCO}_3)_2$ ).

Although the physical and chemical properties of several types of wood ash are well known (e.g., Etiégni and Campbell 1991), less is known of residential wood ash. In addition, no field or laboratory experiments have been conducted to evaluate the solubility of residential wood ash in soft water lakes. These lakes are nutrient-poor with low capacity to buffer acid deposition due to the underlying bedrock (Arp et al. 1996; Jeffries and Snyder 1983) that can be found in the Muskoka region.

Here, we present the results of a laboratory experiment that examined the solubility of residential wood ash in soft water media that typify Canadian Shield lakes. The experiment was designed to determine if wood ash types (e.g., hardwood) varied in readily extractable nutrients.

## **MATERIALS AND METHODS**

### ***Experimental design***

To assess the solubility of wood ash, we conducted a laboratory experiment at the Ministry of the Environment and Climate Change (MOECC), Dorset Environmental Science Centre (DESC), Dorset, Ontario between June 21<sup>st</sup> and July 21<sup>st</sup>, 2017.

In our experiment, in 70 Mason jars, we suspended 1 g of pre-weighed wood ash in 400 ml of FLAMES media, a medium designed to reflect the major ion chemistry of Red Chalk and Blue Chalk lakes, two soft water Canadian Shield lakes with abundant and stable plankton communities (Celis-Salgado et al. 2008). We used three wood ash types in our experiment: hardwood, hardwood-softwood mix, and wood pellet. Within each ash type, we used three

sources of hardwood and hardwood-softwood mix (n=30 each), and one source of wood pellet (n=10). The Mason jars were partially covered with Parafilm<sup>8</sup> to reduce the rate of evapotranspiration and shaken once a week to partially simulate disturbance such as a weekly rainfall.

### ***Sampling protocol***

Media samples were collected on Day 1, 6, 9, 16, and 30 from 14 jars (2 wood pellet, 6 hardwood, and 6 hardwood-softwood mix). The media was filtered through a Supor-200 membrane disc filter (0.2 µm pore size, 47 mm diameter; PALL Life Sciences, Michigan, USA) to remove ash particles and analysed for pH, alkalinity, conductivity, cations, anions, phosphorus, and nitrogen species (ammonium, nitrates, and organic nitrogen + ammonium) at the MOECC, DESC Chemistry Laboratory. Following filtration, we dried the wet ash remaining in the Mason jar at 250 °C using a Conventional Oven (Despatch Industries, model# LEB1-27) for six to seven hours and re-weighed.

Here, we report the results on the major nutrients obtained from the chemical analysis of the media that contained the soluble component of nutrients that dissolved from the wood ash.

## **RESULTS**

In general, wood ash types varied in available nutrients. On average, we detected much higher levels of soluble Ca in wood pellet ash on Day 1 (~85 mg/g of ash) when compared to

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<sup>8</sup> A trademark for any thermoplastic material manufactured as sheets or membranes etc. for wrapping or sealing (Oxford Dictionary)

hardwood (mean 1.4 mg/g of ash) and hardwood-softwood mix (mean 1.6 mg/g of ash). This trend was not evident by the end of the experiment, i.e., Day 30. Instead, we observed the opposite, where mean Ca levels were higher in hardwood (~4 mg/g of ash) and hardwood-softwood (~5 mg/g of ash) when compared to wood pellet samples (~2 mg/g of ash) (Figure 3.1).

By the end of the experiment (Day 30), on average, soluble potassium levels were found to be higher in hardwood (~87 mg/g of ash) and hardwood-softwood mix (mean 97 mg/g of ash) when compared to wood pellet (mean ~64 mg/g of ash) (Figure 3.2).

Like potassium, we detected a similar pattern with soluble phosphorus where, on average, higher levels were detected on Day 30 for hardwood (~294  $\mu\text{g/g}$  of ash), and hardwood-softwood mix (mean ~296  $\mu\text{g/g}$  of ash) when compared to wood pellet (mean ~155  $\mu\text{g/g}$  of ash) (Figure 3.3) (Note that phosphorus units are in  $\mu\text{g/g}$  not mg/g).

We also observed higher mean levels of soluble magnesium on Day 30, in hardwood-softwood mix (~9 mg/g of ash) when compared to hardwood (mean 7 mg/g of ash) and wood pellet (mean ~6 mg/g of ash) (Figure 3.4).

## **DISCUSSION**

Our experiment was designed to assess the solubility of different wood ash types. We observed that wood ash types varied in their solubility of major nutrients. Wood pellet contained the highest amount of Ca on Day 1 when compared to the other wood ash types. This result was not surprising as in Chapter 2, we discovered that wood pellet contained 37% of Ca. However, we did not expect the loss of Ca over time as observed by Day 30 of the

experiment. From the chemical analysis, wood pellet media on Day 1 was saturated<sup>9</sup> with respect to Ca, as the Ca level recorded was, on average, 271 mg/L, which is 179% higher than the recorded solubility of CaCO<sub>3</sub> (15 mg/L). By Day 30, average Ca levels were 4.73 mg/L or ~2 mg/g of ash, of which only 0.2% of the Ca would be soluble. As we did not change the overlying media between Day 1 and Day 30, we believe that the Ca in the wood pellet media rebound to the ash sediments or plated out on the walls of the Mason jar, or formed a particulate that was removed during filtration. The plating of the Mason jar is likely as we observed a white precipitate, possibly CaCO<sub>3</sub>, on all the jars containing wood pellet ash. Nonetheless, the high level of Ca on Day 1 observed for wood pellet suggests that this ash type could be used to obtain an initial pulse of Ca to Muskoka forests and lakes.

For hardwood and hardwood-softwood mix of ash, the release of Ca appears to occur much more slowly when compared to wood pellet ash. By Day 30, there was 0.4% to 0.5% of soluble Ca available and on average, the Ca levels ranged from ~11 mg/L to 12 mg/L for both ash types. The Ca concentrations observed suggest that the media containing hardwood and hardwood-softwood mix of ash was close to saturation (as lower than 15 mg/L) despite having low solubility levels. This is promising for Muskoka where hardwood tree species are mainly burnt as it suggests the hardwood ash would be a useful long-term source of Ca.

We did not expect to observe higher levels of potassium by Day 30 when compared to Ca. By the end of the experiment, all wood ash types had potassium levels > 150 mg/L, which is 100x the recorded solubility for CaCO<sub>3</sub>. If the potassium found in wood ash is potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) - discussed in Chapter 2 - then this compound is very soluble in water

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<sup>9</sup> Containing the largest possible amount of a particular solute in a solution (Oxford Dictionary)



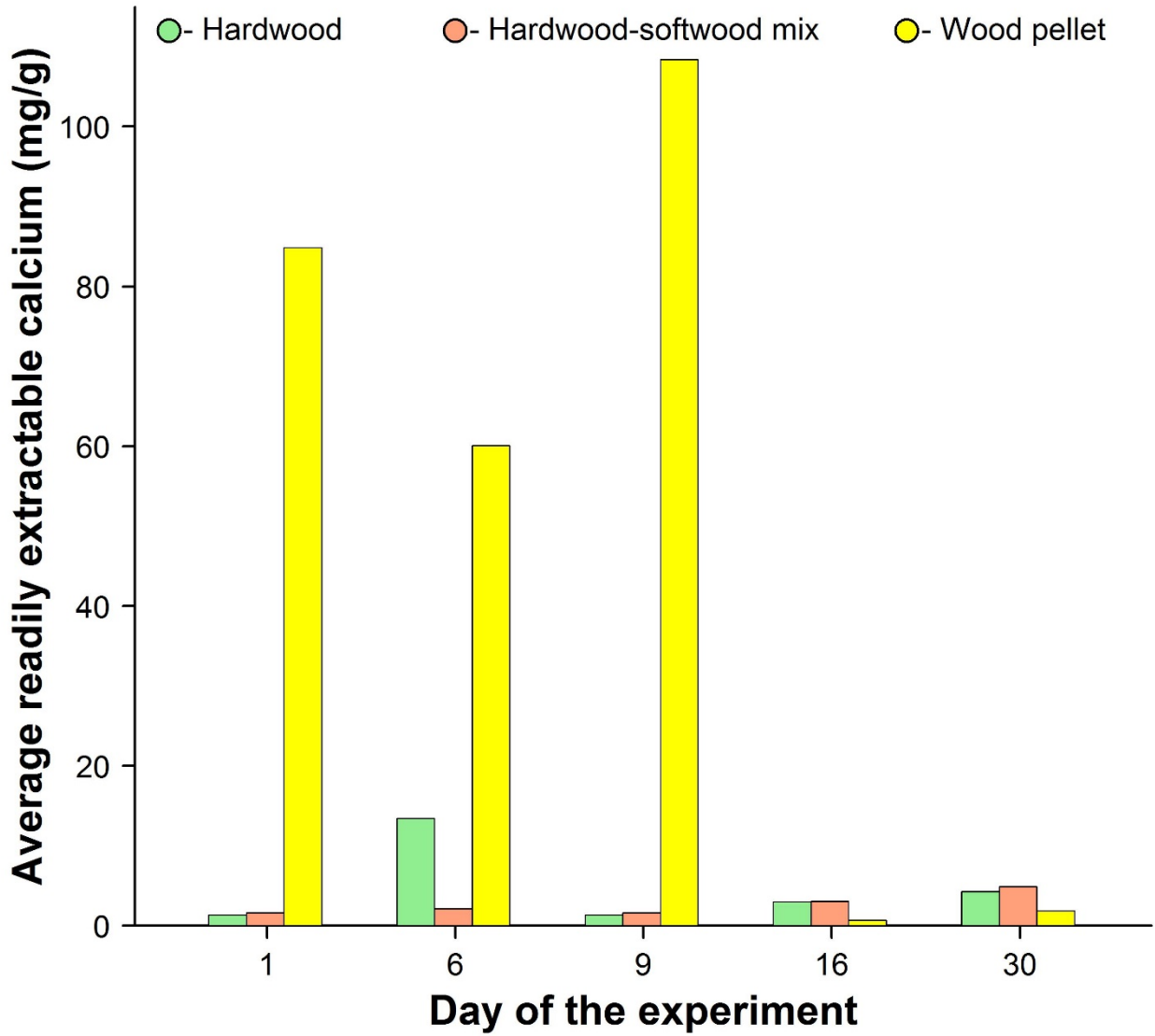
(112 g/100 ml @20°C)<sup>10</sup>, which would explain the high levels of potassium observed, and also suggests that there may be issues with potassium toxicity if residential wood ash is used as a soil additive in Muskoka in the immediate vicinity of the addition. We discuss the risk of potassium toxicity in detail in Chapter 4.

Of the four major nutrients examined, phosphorus, was the least soluble. By Day 30, we only detected between 0.02% and 0.03% of the total phosphorus (TP) as soluble in all wood ash types. In Chapter 2, we detected 0.7% to 0.8% of phosphorus in dry wood ash. These results suggest that only a small fraction of the phosphorus will be leached from wood ash if it is used as a soil additive. However, we noticed that the solubility of phosphorus did not stabilize, as levels increased over time. While only a small fraction of the TP in the wood ash was soluble, this could become an issue for nearby lakes if large amounts of wood ash were applied to watershed soils. We tested this theory by estimating how much phosphorus would be readily available if wood ash was applied at 4000 kg (4 tonnes) per hectare – the minimum application rate that could be used to help solve the Ca decline problem in Muskoka (Carolyn Reid, Trent University, pers. comm.). At 4 tonnes per hectare, about 800 g (0.8 kg) of phosphorus per hectare (Appendix 2) would be readily available to watershed soils, and is roughly equivalent to the natural load from rain and snow of 750 g (0.75 kg) of phosphorus per hectare, recorded annually in Muskoka, east of Huntsville (Nicholls and Cox 1978). By comparison, annual phosphorus loading from forested areas in Muskoka were ~50 g (0.05 kg) per hectare (Dillon and Rigler 1975), which is 175% less than that released from atmospheric deposition. These results suggest that large inputs of phosphorus are not likely

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<sup>10</sup> PubChem, Open Chemistry Database. *Potassium carbonate*  
([https://pubchem.ncbi.nlm.nih.gov/compound/potassium\\_carbonate#section=Solubility](https://pubchem.ncbi.nlm.nih.gov/compound/potassium_carbonate#section=Solubility))

to have major negative impacts on lake ecosystems, especially in watershed soils rich in iron, where phosphorus is not very mobile. Moreover, terrestrial plants will readily gobble up surface applied phosphorus. As a precaution, changes in TP levels in ground and surface waters should be tracked in at least initial wood ash additions plans.



**Figure 3.1.** Mean extractable calcium released over 30d by different wood ash types.

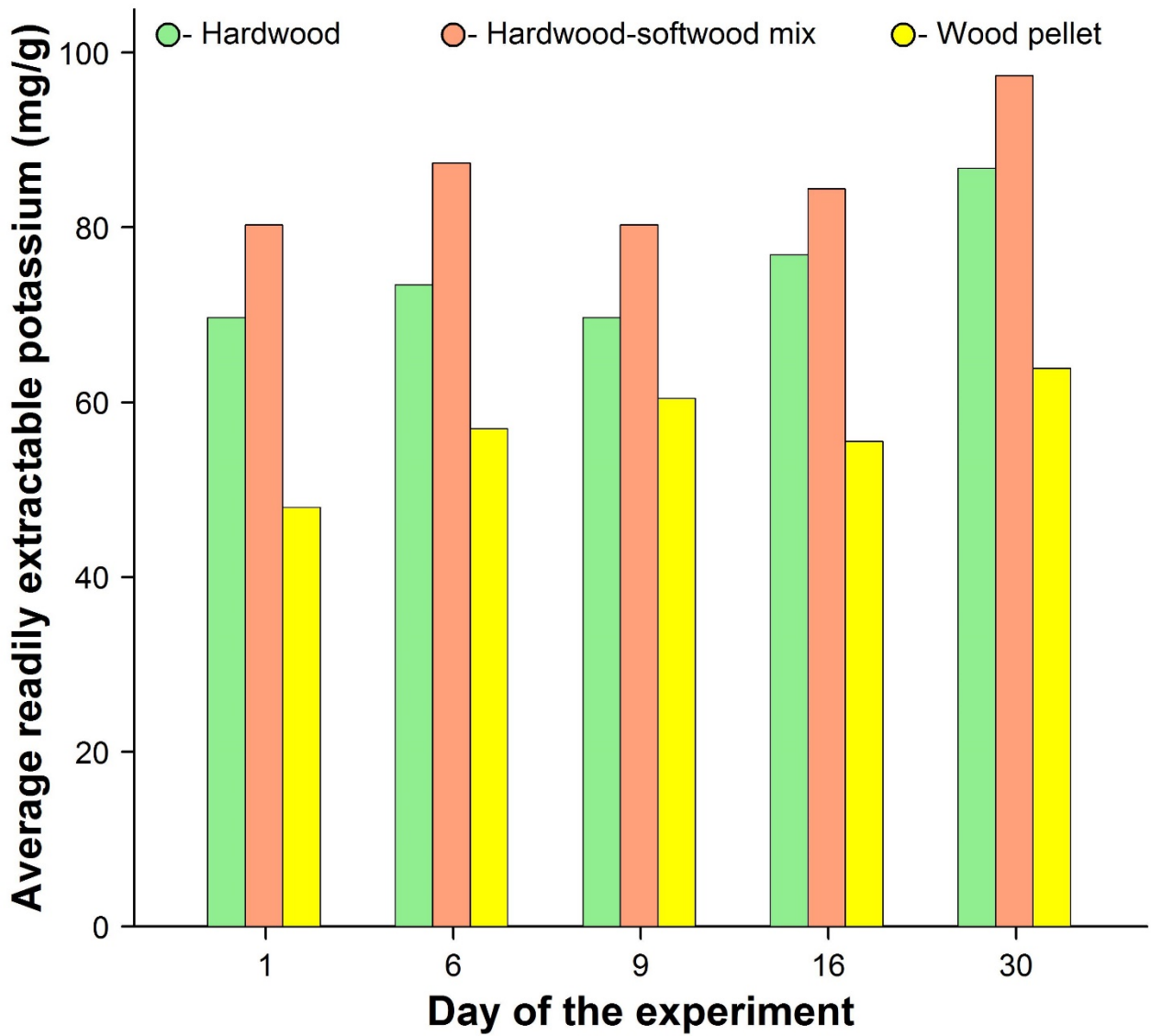


Figure 3.2. Mean extractable potassium released over 30d by different ash types.

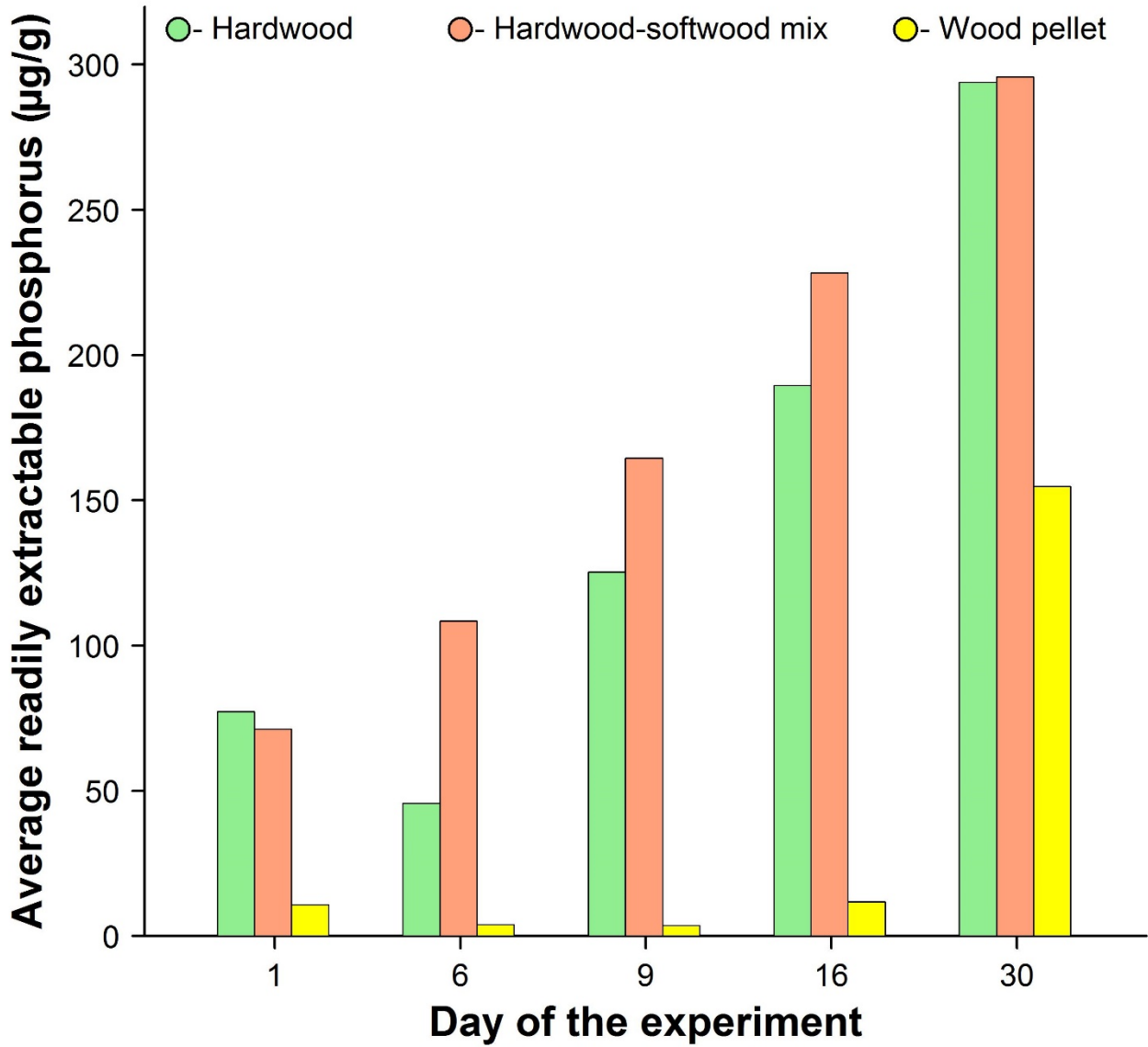


Figure 3.3. Mean extractable phosphorus released over 30d by different ash types.

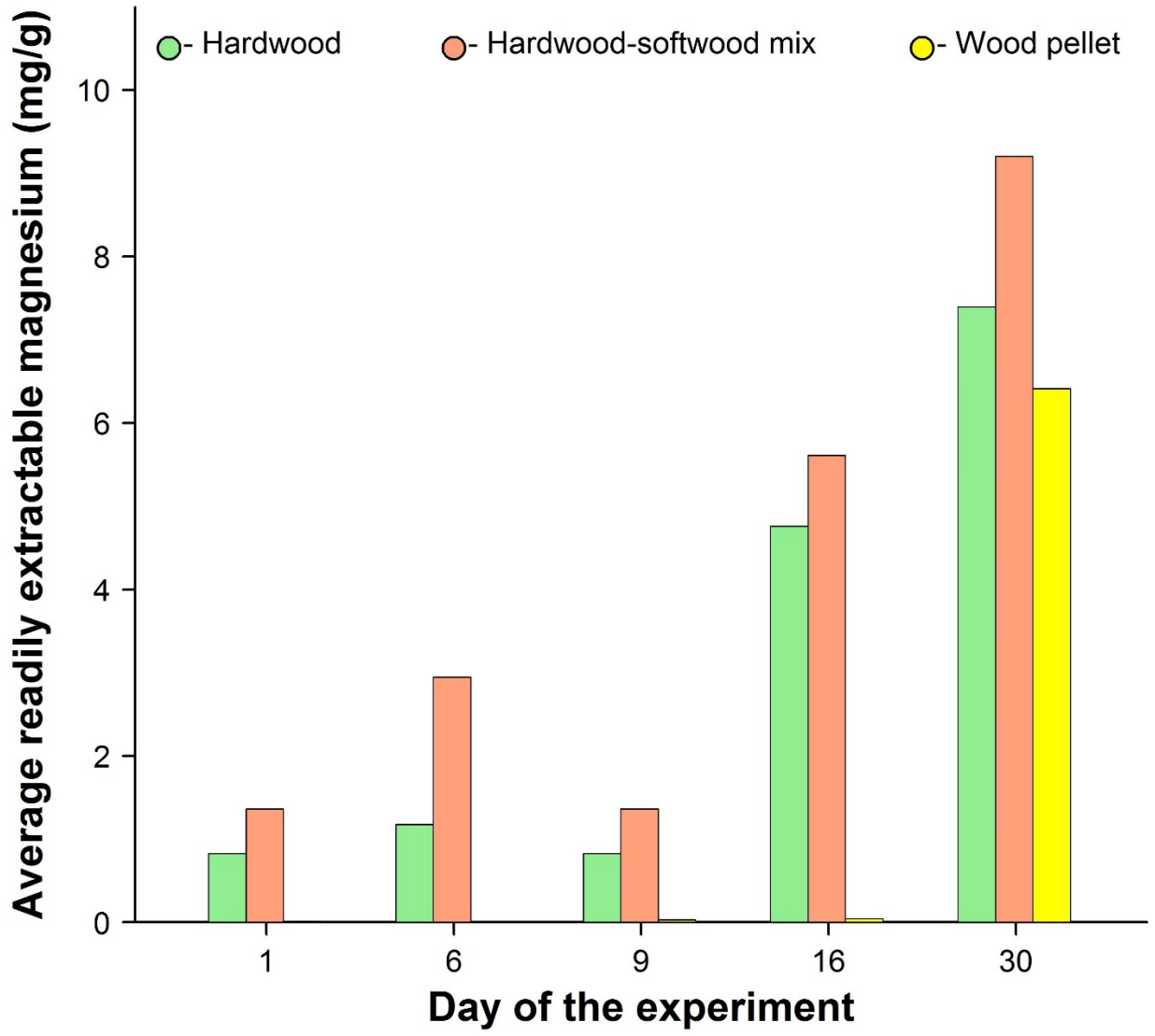


Figure 3.4. Mean extractable magnesium released over 30d by different ash types.

## **Chapter 4**

# **The short-term aquatic toxicity and toxicity of sedimented residue of wood ash to *Daphnia***

## **ABSTRACT**

Wood ash is often generated during the heating season in many homes in Muskoka. Although wood ash is a good source of calcium (Ca) and potassium, the effect of wood ash on aquatic organisms has not been assessed. We conducted two laboratory experiments to determine the toxicity of three residential wood ash types (hardwood, hardwood-softwood mix, and wood pellet) on *Daphnia*, a keystone species of soft water lakes in Muskoka. We used 48 hour bioassays and four treatments (a Concentrate, and 10-, 100-, and 1000-fold dilutions of the concentrate) to examine the short-term aquatic toxicity of wood ash, and a 15 day bioassay to examine the long-term toxicity of wood ash in lake sediments. There was no effect of wood ash type on *Daphnia* survival as high mortality rates were detected using the Concentrate and DF10 for all ash types over 48 hours. The high mortality rates observed were a consequence of a very concentrated elutriate (10% ash) and resultant high potassium levels that rapidly disappeared with dilution. There was also no effect of wood ash type on *Daphnia* fecundity or rate of maturation in the longer term bioassays. While some toxic effects are expected if residential wood ash was concentrated in one spot, this toxicity would decline rapidly in space as wood ash was diluted with sinking and mixing in Muskoka lakes.

## **INTRODUCTION**

Wood ash – the residue from the combustion of wood – is generated in fairly large quantities during the heating season in Muskoka, and elsewhere in temperate latitudes around the world. Currently, wood ash is treated as a waste product in Canada and landfilled at a cost to the municipality and society at large. However, wood ash can be used as a soil liming agent (Lickacz 2002), and as a fertiliser, as it contains nutrients required by plants (e.g., Ca,



magnesium, potassium and phosphorus) (Perry n.d.). When applied to forest soils, wood ash has improved tree growth on sites where nitrogen is not limiting (Wang et al. 2007; Brais et al. 2005), and increased the levels of Ca in the leaves (Augusto 2008) and soil (Brais et al. 2005).

While the application of wood ash to forests appears to have positive impacts, no field or laboratory experiments have been conducted to evaluate the impacts wood ash might have on aquatic ecosystems. For example, impacts on the “white rat” of aquatic toxicology, the water flea, *Daphnia*. In Chapter 2, we suggested that metal levels in residential wood ash are unlikely to pose a problem to our lakes, and here we test that presumption. To date, the effects of wood ash on aquatic organisms are limited to phytoplankton, where increased biomass was detected in 2 small humic<sup>11</sup> headwater lakes in southern Finland following wood ash application to their subcatchments (Tulonen et al. 2002). However, based on the effects of wood ash on phytoplankton, we are unable to predict how wood ash might affect crustacean zooplankton.

Here, we present the results of laboratory toxicity bioassays that examined the (1) short-term aquatic effects of wood ash elutriate<sup>12</sup> and (2) long-term effects of sedimented wood ash on *Daphnia*. Daphniids have been primarily used in toxicity bioassays because they (1) have a short life cycle; (2) are relatively easy to culture in the laboratory; (3) reproduce asexually so clones can be kept for extended periods in the laboratory; and (4) are sensitive to environmental changes and a broad range of aquatic contaminants. Overall, *Daphnia* is a

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<sup>11</sup> Humic or dystrophic lakes contain high amounts of humic substances (e.g., organic matter, peat, coal) and organic acids. You can read more about these lakes @ <https://www.muskokawatershed.org/blog/pt3-tea-stained/>

<sup>12</sup> Aqueous solution obtained from adding water to a solid waste, shaking the mixture, then filtering it (Adapted from 'Acute lethality test using *Daphnia* spp.')

keystone species<sup>13</sup> of most freshwater habitats (e.g., lakes and ponds), and provides an important link between primary producers (e.g., algae), and higher trophic levels (e.g., fish) (Lampert 2006).

## **MATERIALS AND METHODS**

To assess the effect of wood ash elutriate on *Daphnia*, we used iso-female<sup>14</sup> lines of *Daphnia pulicaria* that were collected in 2006 from Red Chalk Lake, located in the Muskoka region. This region, located in south-central Ontario, is characterized by lakes that are oligotrophic or nutrient-poor with low capacity to buffer acid deposition due to the underlying bedrock (Arp et al. 1996; Jeffries and Snyder 1983).

### ***Daphniid cultures***

*Daphnia* were maintained in stock cultures in the Field Laboratory for the Assessment of Multiple Ecological Stressors (FLAMES) located at the Ministry of Environment and Climate Change (MOECC), Dorset Environmental Science Centre (DESC), Dorset, Ontario. *Daphnia* were cultured in FLAMES media; a media based on the water chemistry of two freshwater lakes: Red Chalk and Blue Chalk (Celis-Salgado et al. 2008) that have maintained stable biodiverse zooplankton assemblages. Water was changed once or twice a week, with fresh algae (*Pseudokirchneriella subcapitata*) and media being added at a ratio of about 40% (old) to 60% (new) media. Stock populations were housed in Conviron growth chambers (Model E7/2) on a 16:8 light dark cycle at 20°C.

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<sup>13</sup> A species on which other species in an ecosystem largely depend, such that if it were removed, the ecosystem would change drastically (Oxford Dictionary)

<sup>14</sup> Originating from a single female

## **A. SHORT-TERM TOXICITY EXPERIMENT**

### ***Elutriate preparation***

Elutriate was prepared by adding 150 g of wood ash, i.e., hardwood, hardwood-softwood mix, and wood pellet to 1.5 L of FLAMES media (equivalent to a 10% wood ash solution) and shaking the mixture for 2 hours and 18 minutes on a rotary shaker (Fermentation Design Inc., Allentown, PA) (Figure 4.1). This time period was determined from ash sedimentation rates and represented our estimate of how long the ash would remain in the surface mixed layer of a typically-sized Muskoka lake. The elutriate was filtered through a Supor-200 membrane disc filter (0.2 µm pore size, 47 mm diameter; PALL Life Sciences, Michigan, USA) to remove ash particles. The elutriate was then autoclaved at 250°C for 30 minutes to eliminate any possible biological contamination prior to use in FLAMES – a “clean” laboratory.

We created three additional concentrations by diluting the elutriate concentrate (hereafter referred to as “Concentrate”) with FLAMES media by factors of 10. Based on this, the four concentrations used in our experiment were the Concentrate, DF10, DF100, and DF1000. A 500ml subsample of each concentration created from hardwood, hardwood-softwood mix, and wood pellet ash was analysed for pH, alkalinity, conductivity, cations, anions, phosphorus, nitrogen species (ammonium, nitrates, and organic nitrogen + ammonium), and dissolved inorganic carbon (Appendix 1) at the MOECC, DESC Chemistry Laboratory.

## ***Experimental design***

Prior to initiating experimental trials, we isolated 30 *Daphnia pulicaria* neonates from a Red Chalk iso-female line into 40 ml glass vials containing FLAMES media and algae. Vials were examined daily for neonates. Toxicity experiments using hardwood (n=120), hardwood-softwood mix (n=120), and wood pellet (n=40) ash were initiated using neonates (<24 hours old). Ten *Daphnia* neonates were exposed to each wood ash elutriate concentration (as described above) in 40 ml glass vials over 48 hours. We used 48 hours in accordance with test conditions stipulated for conducting “Acute Lethality Tests using *Daphnia* spp.” (Environment Canada, 1990). No food was added during the 48 hours. A small flake of cetyl alcohol [CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>OH] was also added to the surface of each vial to prevent *Daphnia* neonates from becoming entrapped in surface film. All toxicity experiments were conducted in two Percival Incubators (Model GR36L) at 20°C on a 16:8 light dark cycle. Neonate survival was recorded every 24 and 48 hours following commencement of the experiment.

## **B. LONG-TERM TOXICITY EXPERIMENT**

Having shown that wood ash dissolves slowly and differentially in waters, we wished to test the possibility of longer term toxicity from sedimented wood ash residues. We established a 15 day experiment on August 10<sup>th</sup> to assess the toxicity of this sedimented wood ash residue to *Daphnia*. We added 1 g of hardwood, hardwood-softwood mix, and wood pellet ash to 250 ml FLAMES media in 45, 500 ml Mason jars and shook the mixture for 2 hours and 18 minutes. Once shaken, the supernatant<sup>15</sup> was decanted and fresh FLAMES media added (i.e., 250 ml). We assumed the decanted and discarded supernatant captured the readily soluble

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<sup>15</sup> Supernatant is the liquid lying above a solid residue after conducting a process (e.g., centrifugation) (Oxford Dictionary)

ash constituents that would be dissolved into the surface mixed layers of a lake, while the residual ash – what this experiment used – reflected the residual ash that would settle to lake sediments. The jars' contents were allowed to settle for 5 hours prior to the addition of “baskets” – Plexiglas with 130 µm mesh glued to the bottom of the cylinders. The “baskets” were held in place in each Mason jar using an elastic band and two paper clips (Figure 4.2). *Daphnia* neonates were added to each “basket” in a Mason jar. Neonates were not fed for the initial 48 hours to allow a comparison with short-term toxicity experiments. Animals were then fed 0.25 ml of *Pseudokirchneriella subcapitata* three or four times a week until the end of the experiment on August 25<sup>th</sup>. Survival and reproduction were recorded daily.

## **RESULTS**

### ***Short-term toxicity***

Overall, neonate survival over 48 hours was not influenced by the wood ash type. For all wood types used, we detected a 100% mortality rate amongst the neonates when using the Concentrate and a dilution factor of 10 (i.e., DF10). In addition, we observed 100% survival of neonates while using the hardwood elutriate created from dilution factors of 100 and 1000 (DF100 and DF1000 respectively). For the same concentrations, we detected increased survival from 60% to 100% using the hardwood-softwood elutriate and from 90% to 100% using the wood pellet elutriate (Figure 4.3).

## ***Long-term toxicity***

### ***Survival***

Neonate survival over 15 days was somewhat influenced by the wood ash type. In the first 48 hours, we detected 100% mortality amongst neonates exposed to wood pellet ash, similar to that observed in the short-term assay. It is likely that all neonates died within 24 hours of exposure. In contrast, we observed a 100% and 80% survival rate in neonates exposed to hardwood and hardwood-softwood mix of ash, respectively, over 48 hours. This trend was not evident by Day 15 as mean survival rates for neonates exposed to hardwood-softwood mix and hardwood ash had declined to 53% and 83%, respectively. A similar mean survival rate of 83% was also observed in neonates exposed to FLAMES media alone that represented our “Control” (Figure 4.4).

### ***Number of neonates produced***

Sedimented wood ash did not influence neonate production<sup>16</sup>. On average, about 17 *Daphnia* neonates were produced per mature individual over 15 days of the experiment in both the hardwood ash and Control. In contrast, neonate production was 43% lower (~11 neonates) in the hardwood-softwood mix of ash. As all neonates exposed to wood pellet ash died within 24 hours of exposure, they produced no offsprings (Figure 4.5).

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<sup>16</sup> Neonate production refers to the ability of a mature *Daphnia* individual to produce neonates while exposed to a treatment

### Age at maturation

Like neonate production, sedimented wood ash did not influence the maturation rate of *Daphnia* individuals. On average, *Daphnia* mothers exposed to hardwood and hardwood-softwood mix of ash produced their first clutch<sup>17</sup> at 8 days old when compared to the Control that reproduced at 9 days old. Second and third reproduction occurred at 11 days and 12 days, respectively, for hardwood ash and at 10 days and 11 days, respectively, for hardwood-softwood mix of ash (Figure 4.6). *Daphnia* neonates exposed to wood pellet ash did not mature as they died within 24 hours of exposure.

## **DISCUSSION**

Our experiment was designed to assess the short-term and long-term toxicity of wood ash to *Daphnia*, a keystone species present in Muskoka lakes. We observed surface water toxicity of two wood ash treatments and minimal toxicity of sedimented ash on *Daphnia* neonates. Although the wood ash Concentrate or elutriate and 10 fold dilution treatment were toxic, this toxicity was a function of how much ash was used to prepare the elutriate, i.e., 150 g, as well as the high potassium levels observed (discussed below). If, by contrast, wood ash was applied directly to lakes and settled to the sediments, there would be no toxic effects on *Daphnia* survival and reproduction using hardwood, hardwood-softwood mix, or wood pellet ash, as the wood ash concentrations would be much lower than those we used. The concentrations of problematic materials extracted from the ash would simply be too low.

High mortality rates detected when using the Concentrate and DF10 treatment could be attributed to either the pH or the concentration of elements present within the wood ash.

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<sup>17</sup> A clutch is a group of eggs fertilized at the same time and laid in a single session (Oxford Dictionary)

The pH of the concentrated elutriates used in our experiment ranged between 10 and 12 and supports Lickacz (2002) findings that wood ash is alkaline and can be used as a liming agent. To determine if the high pH of wood ash elutriate observed contributed to the mortality rates observed, we repeated the experiments, lowering the pH of all elutriates, i.e., hardwood, hardwood-softwood mix, and wood pellet to 8, a pH that is representative of hard water lakes<sup>18</sup> in Ontario. Surprisingly, we concluded that high pH was not the cause of the mortality observed in half of the treatments as 100% mortality was also detected in neonates exposed to both hardwood and hardwood-softwood mix treatments of the Concentrate and DF10 (Figure 4.7) after pH adjustment. Although we detected some survival (40% - 60%) when using wood pellet ash, we believe that pH was not the contributing factor. The cause of mortality was potassium.

Plants require potassium for growth and reproduction. Mammals like you and me need potassium to enhance muscle strength, relieve us from stress, blood pressure, heart and kidney disorders, maintain water balance, and help with our nervous system. Thus, potassium is an essential element for both plants and animals, but there can be too much of a good thing. In *Daphnia*, exposure to high levels of potassium would result in a lowering of the heart rate and eventually, death. Moreover, we had observed high levels of potassium in our solubility trials (see Chapter 3). To test the hypothesis that potassium was the toxic element in the Concentrate and DF10 treatment, we: 1) conducted a 48 hour bioassay using potassium chloride (KCL) at five concentrations (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L); and 2) compared our elutriate chemistry results to published LC50 for potassium using *Daphnia* under similar laboratory conditions. We detected 100% survival

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<sup>18</sup> Lakes that have high mineral content (e.g., calcium and magnesium carbonates)



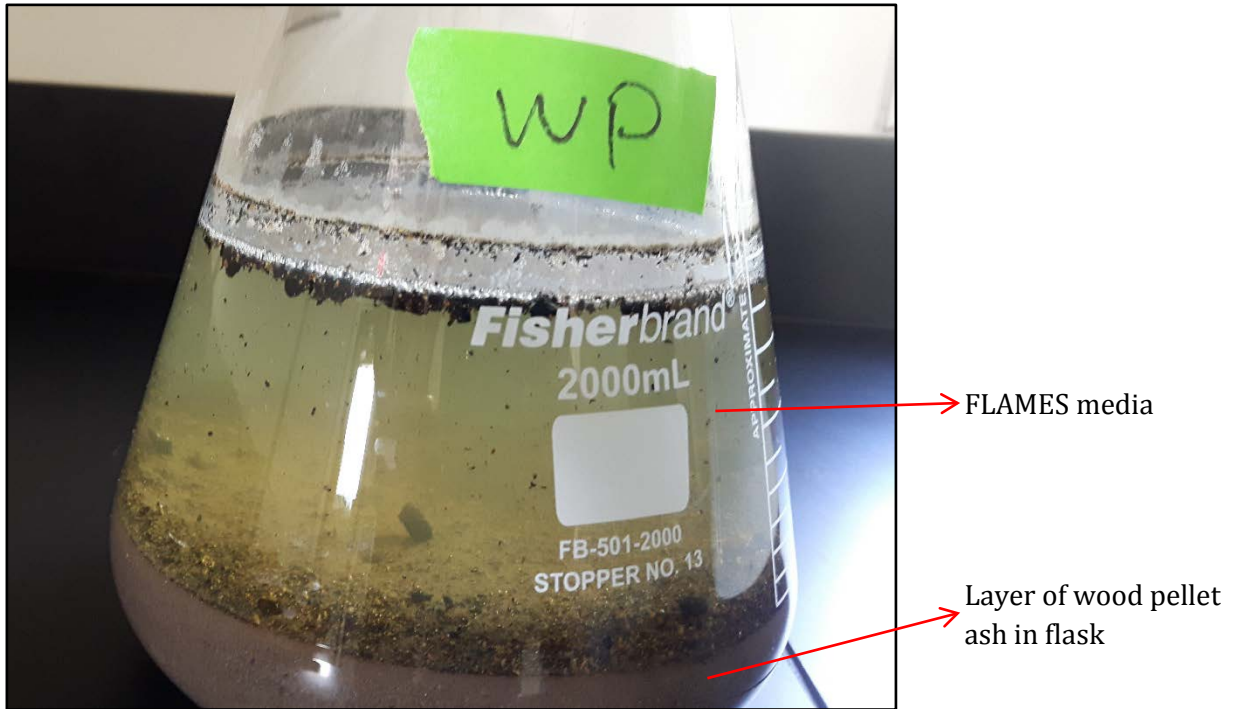
in all KCL treatments with the exception of 250 mg/L, where all *Daphnia* neonates died, suggesting an acute potassium LC50 for our daphniid clone between 200 mg/L and 250 mg/L. Also, most of the potassium concentrations in our Concentrate and DF10 treatment were more than three times that documented in the literature (see Biesinger and Christensen 1972) as being acutely toxic to *Daphnia* (Table 4.1). These findings support our hypothesis that high potassium levels were sufficient to be the cause of the mortalities observed in our 48 hour bioassays. High potassium levels might also explain why *Daphnia* neonates exposed to wood pellet ash over 15 days did not survive, despite the initial removal of the supernatant prior to the start of the experiment. One hypothesis is that potassium is tightly bound in wood pellet and might be slowly released over time. From our solubility experiment, we observed a 15% increase of readily extractable potassium between Day 1 (48 mg/g) and Day 16 (55 mg/g) in wood pellet ash. This increase supports our hypothesis that potassium is slowly released over time. Moreover, 55 mg/g is equivalent to  $55 \times 10^3$  mg/L, which is much higher (>200 fold) than our estimated LC50 of 230 mg/L for *Daphnia* neonates exposed to potassium in the laboratory.

Although the sedimented ash toxicity experiment suggested that wood pellet would cause some toxicity to *Daphnia*, our findings does not reflect what is likely to happen in nature. In nature, any toxicity of ash leachates is likely to dissipate in time and space quickly as wood ash settles and lake waters circulate. To further understand the long-term effects of wood pellet ash, we suggest additional experiments be conducted to determine the responses of *Daphnia*, and perhaps other biota, to potassium under a variety of conditions.

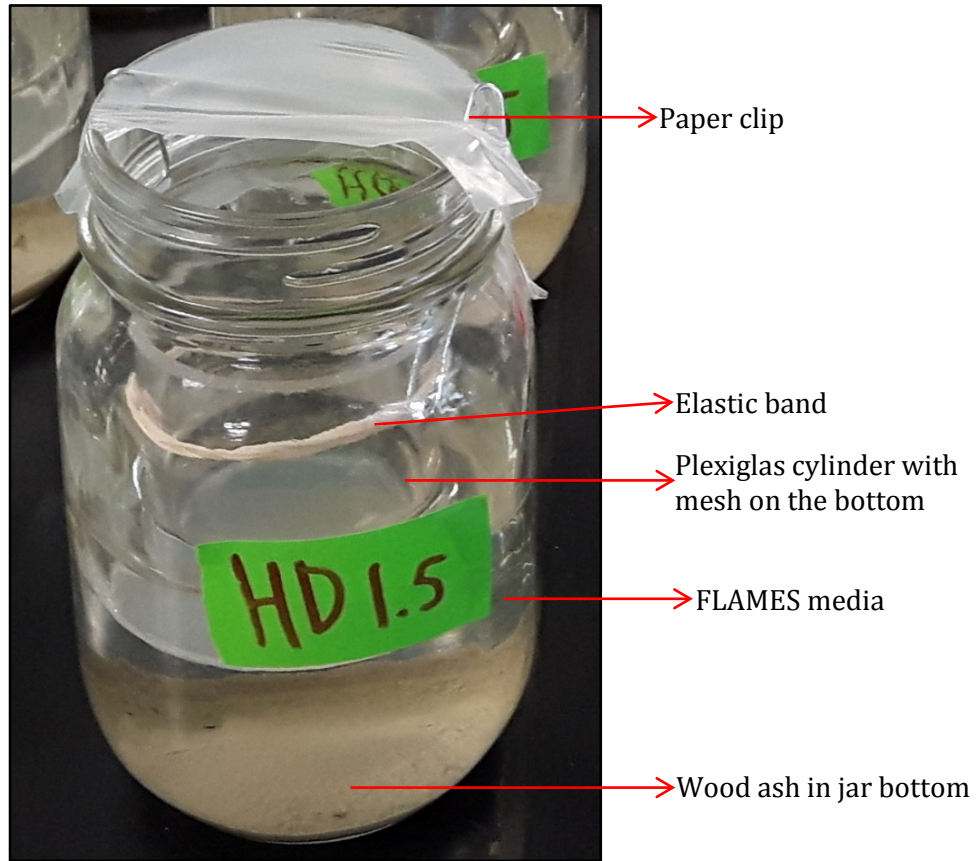
**Table 4.1.** Potassium concentrations in the Concentrate and a dilution factor of 10 compared to the acute toxicity level (93 mg/L) identified for *Daphnia* by Biesinger and Christensen (1972) under similar laboratory conditions

Ash type	Treatment	Concentration of potassium in treatment (mg/L)
Hardwood 1	Concentrate	2,699
	DF10	296
Hardwood 2	Concentrate	4219
	DF10	435
Hardwood 3	Concentrate	450
	DF10	449
Hardwood-softwood mix 1	Concentrate	22,074
	DF10	124
Hardwood-softwood mix 2	Concentrate	2,827
	DF10	259
Hardwood-softwood mix 3	Concentrate	5,675
	DF10	548
Wood pellet	Concentrate	3,200
	DF10	320

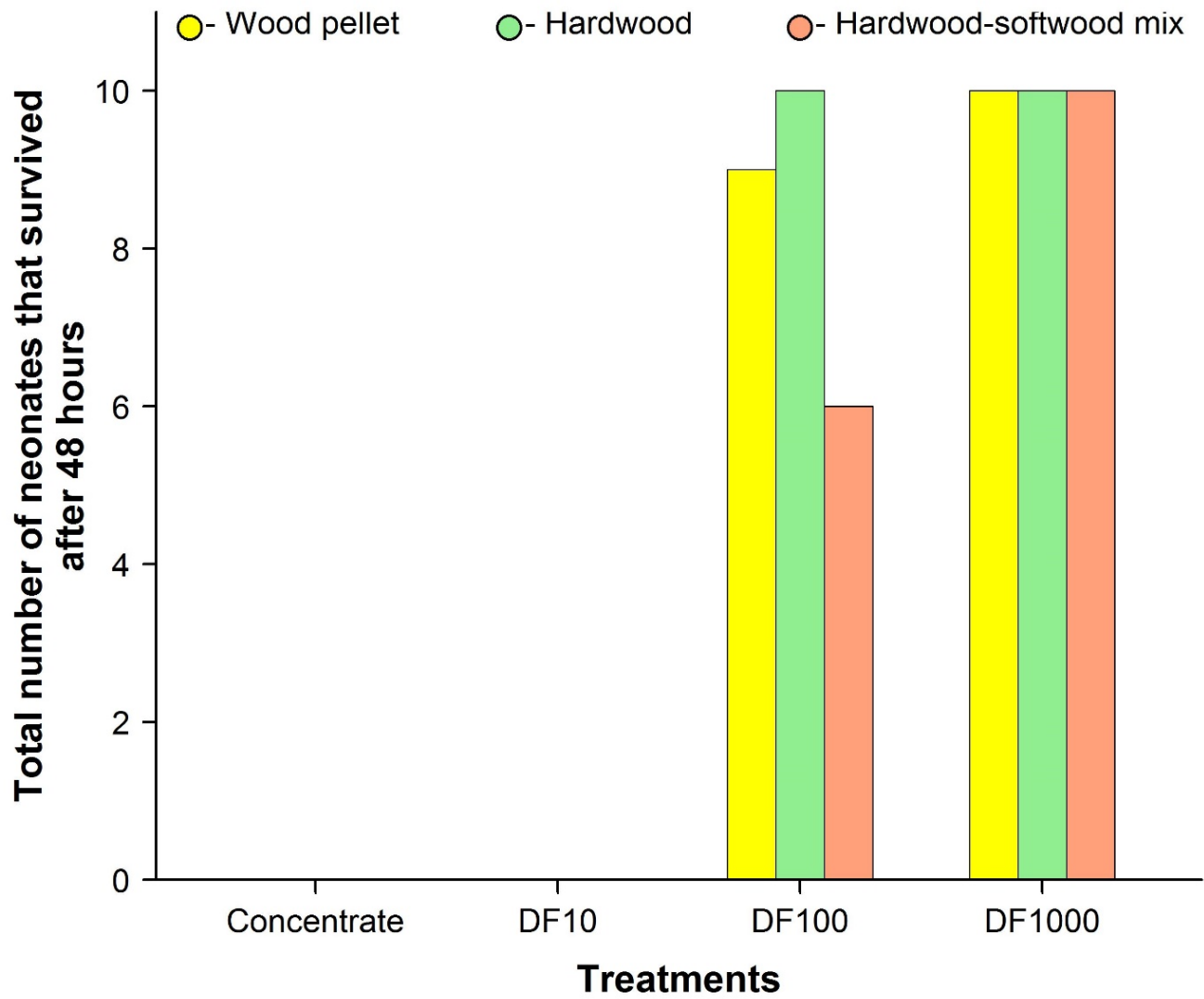
Note: The LC50 is the concentration of material in the water that is estimated to be lethal to 50% of the test organisms. In our 48 hour KCL bioassays, 50% of our daphniid clone died between 200 mg/L and 250 mg/L. We calculated an acute LC50 of potassium to be **230 mg/L**.



**Figure 4.1.** Erlenmeyer flask (2 L) containing 150 g of wood pellet ash and 1.5 L of FLAMES media. (This is an example of the amounts used to form our Concentrate treatments for the bioassays.)



**Figure 4.2.** Mason jar with Plexiglas cylinder used in 15 day toxicity experiment of sedimented ash residue.



**Figure 4.3.** Survival of *Daphnia* neonates after 48 hours in the Concentrate and three dilutions of the three ash types.

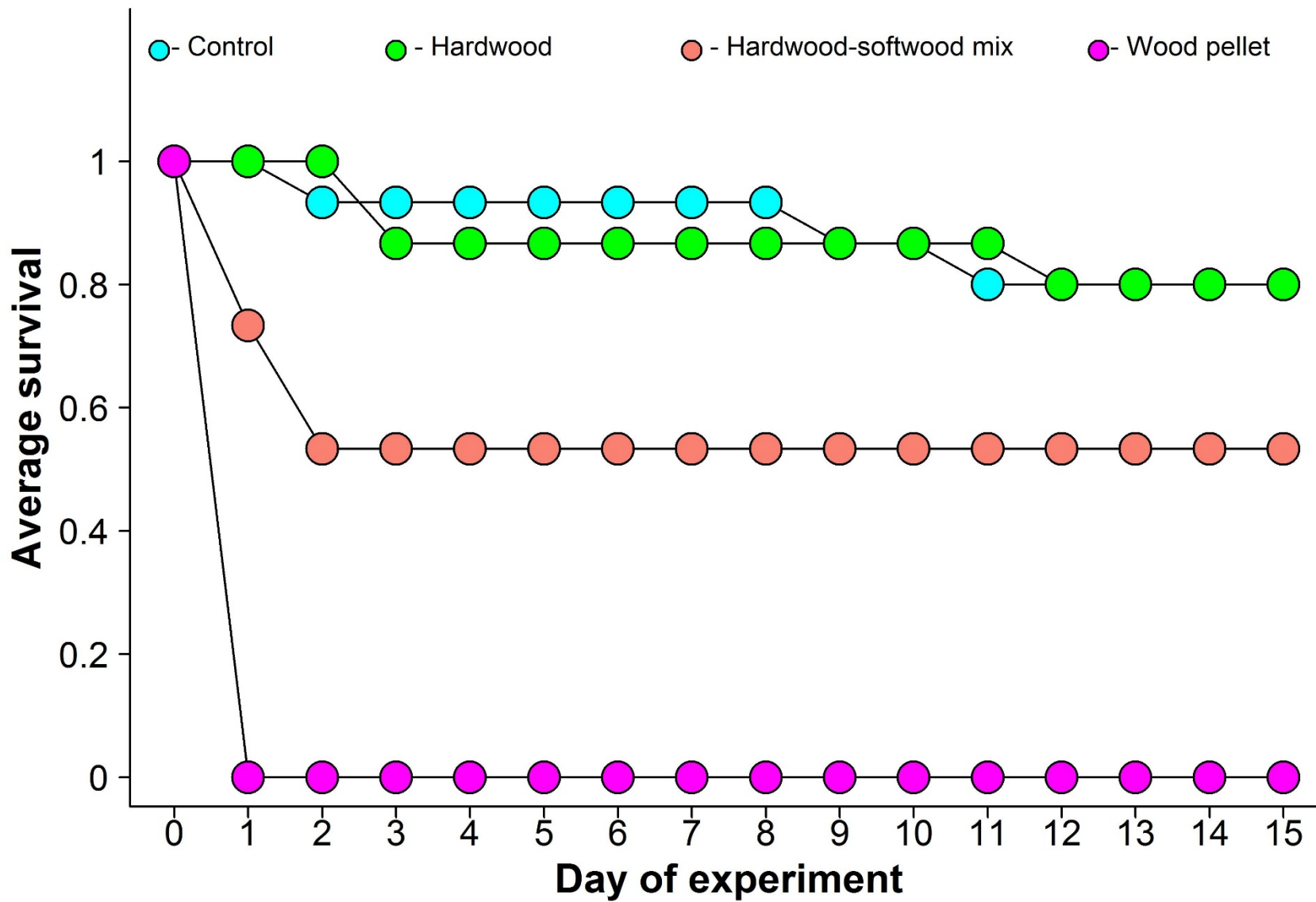
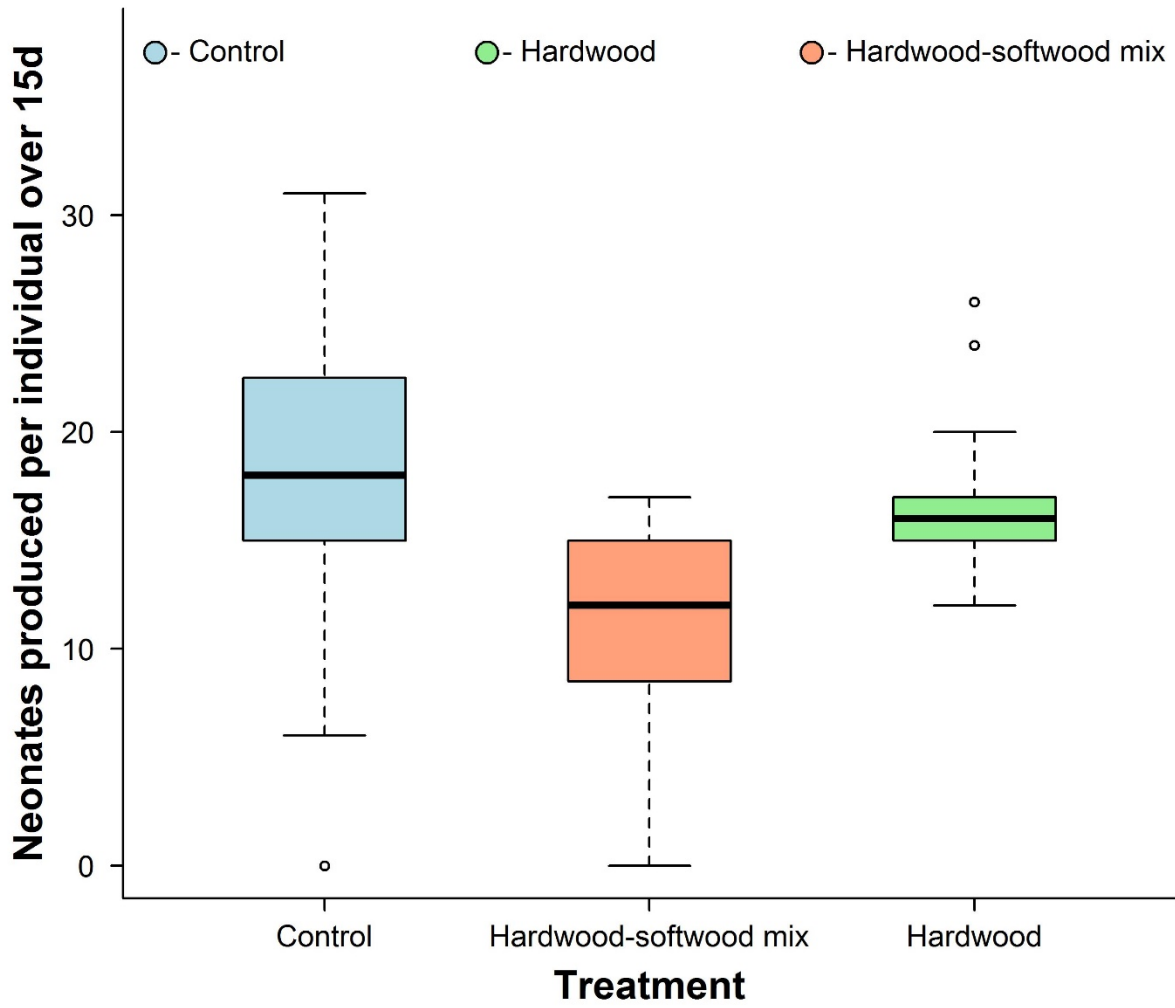
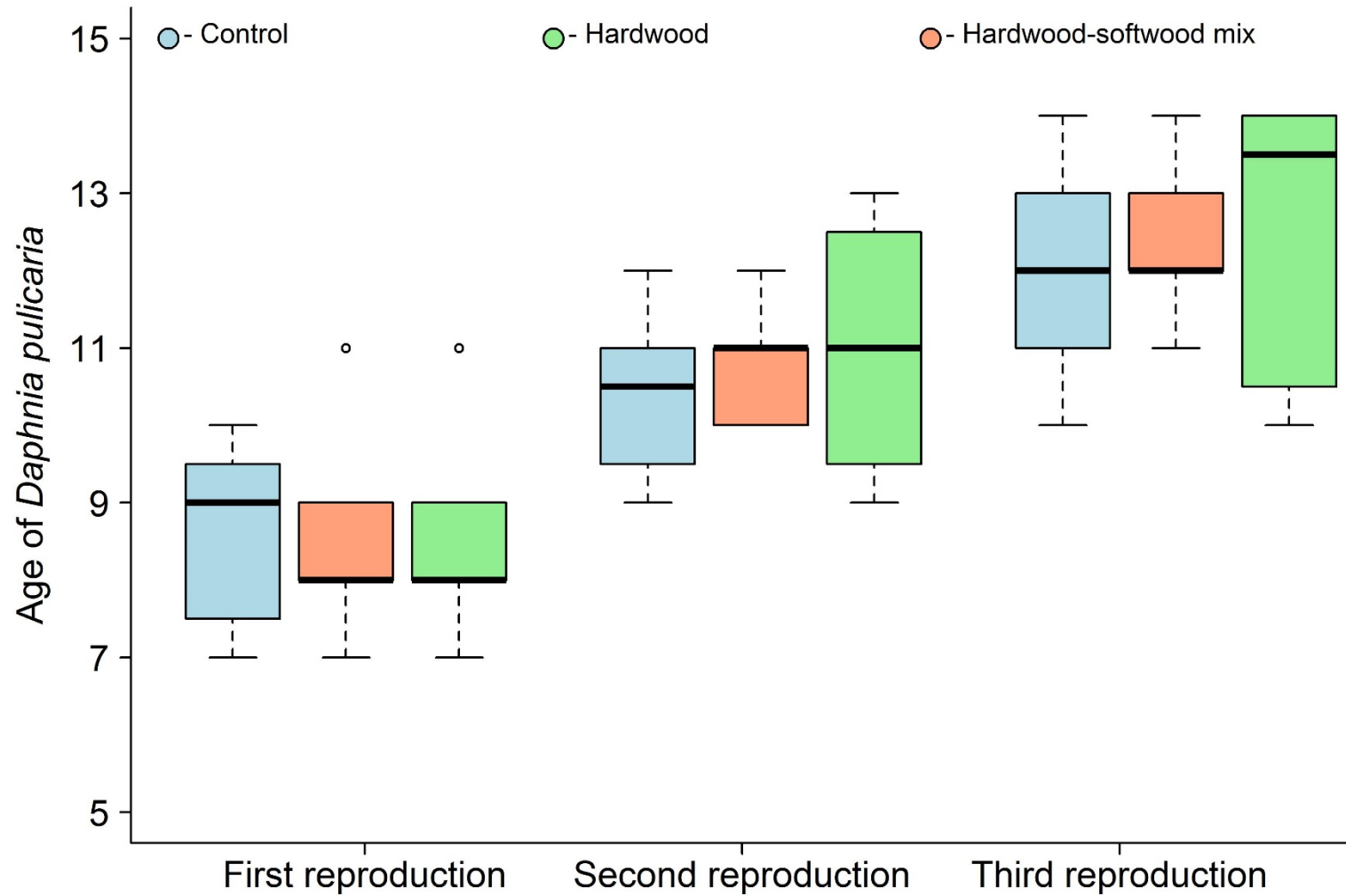


Figure 4.4. Average survival of *Daphnia* neonates exposed to different wood ash treatments over 15 days.



**Figure 4.5.** Box plots of the number of *Daphnia* neonates produced per individual in wood ash treatments. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



**Figure 4.6.** Box plots of the maturation rates of *Daphnia* exposed to different wood ash treatments. The box defines 50% of the observations with the median indicated by the thick horizontal bar. The whiskers delineate 95% of the observations.



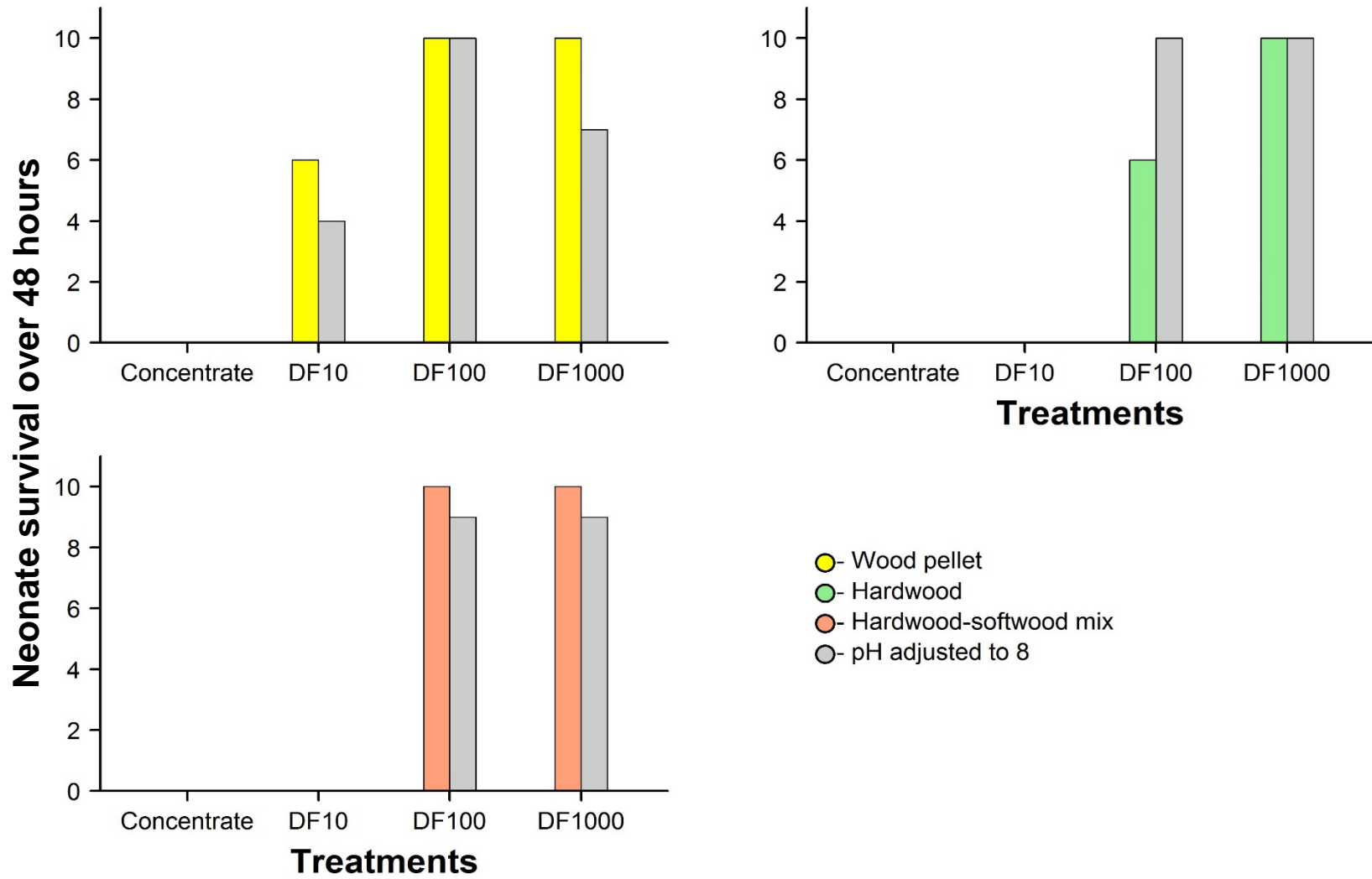


Figure 4.7. Neonate survival when exposed to natural pH in wood ash (10-12) and pH adjusted to 8

## **Chapter 5**

### **Summary and recommendations**

## SUMMARY AND RECOMMENDATIONS

Over the past several decades, Ca decline has emerged as an environmental threat to Muskoka forests and lakes. The resultant damage is all around us – from falling Ca levels in lakes, to slowed sugar maple growth, to decreased abundances of Ca-rich species such as crayfish and the water flea, *Daphnia*. To evaluate the efficacy of residential wood ash to help to solve the Ca decline problem, we conducted several assays and experiments to determine the metal concentrations, the solubility and the short-term and long-term toxicity of residential wood ash. Our results in brief and recommendations are as follows:

- Although residential wood ash contains 11 trace metals, the majority of their concentrations fell well below CM1 level, the threshold for unrestricted land application. Levels of copper and zinc fell at or just above CM1, but well below CM2 levels. None of our residential wood ash samples contained metal concentrations higher than the CM2 level, the latter considered unsuitable for use as a soil additive. Thus, residential wood ash application is unlikely to increase metal concentrations in the soil to levels that might threaten Muskoka forests or lakes.
- Ash from wood pellets contained higher levels of Ca (37%) when compared to hardwood and hardwood-softwood ash (29% - 30%). However, we discovered that wood pellet released its Ca much quicker than the other two ash types. This suggests that wood pellet could be used to obtain an initial pulse of Ca, while hardwood and hardwood-softwood mix of ash might maintain Ca levels over a longer period of time.

- In our toxicity experiments, we observed that wood ash exhibited some toxicity, but this was more evident in the short-term (48 hours) than the long-term (15 days). The observed toxicity was a consequence of our high ash to water media ratios, and surprisingly, was attributable not to metals, nor high pH, but to high levels of the nutrient potassium. Supporting the metal analyses, we do not believe there are toxicity issues in the use of wood ash to manage the low Ca problem in Muskoka lakes, as any local initial toxic effects of high potassium levels in residential wood ash elutriate to *Daphnia* or other aquatic organisms would quickly dissipate, as the ash settled and mixed. As such, we conclude that residential wood ash can be used as a soil amendment and would not be toxic to aquatic animals should it reach lake waters, although the metals and potassium levels in the ash would require ongoing monitoring. It is yet to be determined if there might be any local toxic effects on the plants or animals of forests.

## **Chapter 6**

### **Tips for cottagers and next steps**

### ***Tips for cottagers***

- Do not dispose of your wood ash until it is cold.
- When disposing of wood ash, sprinkle it around trees on your property, especially sugar maple. Do not concentrate the wood ash in any one area.
- Do not apply wood ash from pressure treated wood or wood containing nails, staples, or any other foreign matter to trees on your property. Nails etc. can cause injury to you and your family.
- Do not sprinkle wood ash in any waterbody on or near your property. The forest needs it more and natural processes (e.g., soil leaching) will get Ca to your lakes.

## **Next steps**

With HATSEO now completed, our next steps are to:

- Develop and implement a public education or communication strategy on residential wood ash for stakeholders. The focus will be on species at risk (e.g., sugar maple trees, crayfish) and the benefits of wood ash.
  
- Liaise with different lake and cottage associations to educate them on the value of Muskoka lakes and forests and how they can help protect them.
  
- Solicit media coverage of HATSEO via articles in newspapers, magazines, and lake/cottage association newsletters.
  
- Apply for additional funding to assist with the development and implementation of a large-scale wood ash addition project that would seek to:
  - Test models of wood ash application rates designed to eliminate Ca deficiency in the forest and increase Ca levels in downstream waters;
  - Determine if there are any negative impacts of wood ash addition on the health of forest and lake ecosystems;
  - Build local, agency, and academic interest in solving the Ca decline problem; and
  - Address logistic issues in collecting sufficient wood ash from the public.

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# **APPENDICES**

**Appendix 1.** Chemical characteristics of wood ash elutriate used in 48 hour toxicity experiments. Abbreviations are: total phosphorus (TP), measured in micrograms per litre ( $\mu\text{g/L}$ ); calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulphate ( $\text{SO}_4$ ), dissolved inorganic carbon (DIC), total nitrogen (TN), and gran alkalinity (GAlk), measured in milligrams per litre (mg/L); pH; and conductivity (Cond), measured in microSiemens per centimetre ( $\mu\text{S/cm}$ ).

Ash type	Trtmt	TP ( $\mu\text{g/L}$ )	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	pH	Cl (mg/L)	$\text{SO}_4$ (mg/L)	TN (mg/L)	DIC (mg/L)	GAlk (mg/L)	Cond ( $\mu\text{S/cm}$ )
HWD 1	Concentrate	895.60	0.22	9.09	68.40	2698.67	10.6	143.36	654.69	20.67	298.70	NDUA	7720
	DF10	100.62	2.31	0.74	7.57	295.61	9.3	14.85	71.80	2.50	47.60	250.99	856
	DF100	39.34	2.43	0.01	1.80	35.88	7.6	2.50	17.89	0.59	8.99	37.99	154.30
	DF1000	30.59	2.45	0.71	1.15	13.82	6.8	0.96	10.81	0.34	2.67	10.44	59.10
HWD 2	Concentrate	1422.73	0.15	0.18	19.46	4218.99	11.2	15.96	1022.45	55.86	250.60	NDUA	8910
	DF10	148.39	2.31	0.65	2.87	435.37	9.3	1.89	108.63	6.31	48.05	266.24	983
	DF100	45.81	2.46	0.72	1.28	46.68	7.6	0.78	23.17	1.11	9.54	40.55	174.10
	DF1000	31.55	2.43	0.71	0.99	10.29	6.8	0.56	12.34	0.43	2.80	9.99	62.20
HWD 3	Concentrate	701.88	0.27	0.01	68.62	450	12.5	33.82	394.58	8.63	323.30	NDUA	17140
	DF10	93.65	1.55	0.28	7.62	449.51	10.7	3.28	46.81	1.08	57.03	NDUA	1481
	DF100	38.67	2.44	0.70	1.95	60.36	8.1	0.93	14.32	0.36	16.62	76.95	221
	DF1000	31.92	2.51	0.71	1.22	13.70	7.2	0.69	9.96	0.28	4.34	18.59	73.30
HSD 1	Concentrate	419.24	0.51	66.22	18.65	22074.05	10.1	21.66	640.28	19.67	288.90	NDUA	5830
	DF10	41.22	2.63	2.24	2.76	124.20	8.5	2.35	70.30	1.93	41.35	186.3	641

Ash type	Trtmt	TP (µg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	pH	Cl (mg/L)	SO <sub>4</sub> (mg/L)	TN (mg/L)	DIC (mg/L)	GAlk (mg/L)	Cond (µS/cm)
	DF100	33.48	2.72	2.33	1.26	31.34	7.4	0.80	17.70	0.54	6.69	28.03	122.2
	DF1000	31.60	2.47	0.65	1.14	7.06	6.8	0.52	10.86	0.33	2.26	7.74	50.1
HSD 2	Concentrate	350.18	2.69	108.89	1.38	2827.32	10.2	11.26	843.17	13.69	318.90	NDUA	7120
	DF10	42.54	2.75	0.90	1.28	259.04	8.6	1.39	90.21	1.59	48.74	229.89	785
	DF100	34.26	0.29	0.61	23.04	41.17	7.6	0.70	21.86	0.55	8.93	38.21	154.4
	DF1000	30.90	2.42	0.63	1.13	8.40	6.9	0.42	11.16	0.31	2.37	9.38	55.6
HSD 3	Concentrate	257.81	2.43	2.45	1.05	5675.03	12.6	10.92	1059.10	4.16	285.40	NDUA	21500
	DF10	46.40	2.44	2.64	1.06	547.92	10.9	1.69	113.43	0.64	52.09	NDUA	1805
	DF100	35.84	0.17	0.17	43.44	70.88	8.1	0.57	23.82	0.35	20.31	85.98	264
	DF1000	36.15	0.53	0.53	1.25	17.44	7.2	0.46	12.21	0.30	5.09	20.36	83.6
WP	Concentrate	5.69	18.90	0.01	39.70	3200.00	12.8	54.74	256.48	16.20	11.27	NDUA*	19710
	DF10	12.25	1.30	0.36	11.10	320.00	11.1	6.64	35.52	1.56	36.08	379.90	1240
	DF100	16.39	4.78	0.72	2.33	47.50	8.1	1.56	13.31	0.40	14.35	62.60	182.50
	DF1000	17.02	2.84	0.75	1.04	4.95	6.8	0.60	10.19	0.18	2.13	7.10	45.00

Note: HWD = hardwood ash; HSD = hardwood-softwood mix of ash; WP = wood pellet ash; Trtmt = treatment

\*NDUA = out of range

**Appendix 2.** Calculations to compare phosphorus loading from wood ash application to the land at 4 t/ha with loading to lakes from forested areas, and atmospheric deposition in Muskoka.

### Wood ash application

0.02% of phosphorus was soluble in all three wood ash types

As a proportion, 0.02% = 0.0002

We are applying wood ash at a rate of 4000 kg or 4 tonnes per hectare, therefore:

$$0.0002 \times 4000 \text{ kg} = 0.8 \text{ kg P or } 800 \text{ g P per hectare}$$

### Forested areas

Phosphorus loading is 4.7 or ~5 mg per square metres per year in forested areas (Dillon and Rigler 1975)

Given that 10,000 square metres = 1 hectare, therefore:

$$5 \text{ mg P/m}^2/\text{year} = 50,000 \text{ mg P/ha/year}$$

If we convert 'mg' to 'g' or 'kg', then:

$$50,000 \text{ mg P/ha/year} = 50 \text{ g P/ha/year or } 0.05 \text{ kg P/ha/year}$$

### Atmospheric deposition

Phosphorus loading is 75 mg per square metres per year from rain or snow (Nicholls and Cox 1978)

Given that 10,000 square metres = 1 hectare, therefore:

$$75 \text{ mg P/m}^2/\text{year} = 750,000 \text{ mg P/ha/year}$$

If we convert 'mg' to 'g' or 'kg', then:

$$750,000 \text{ mg P/ha/year} = 750 \text{ g P/ha/year or } 0.75 \text{ kg P/ha/year}$$