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# Cosmogenic Beryllium Cycling in a Natural Forest Setting

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For the degree of Master of Science

Is approved by the final examining committee:

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Head of the Department Graduate Program

Date

COSMOGENIC BERYLLIUM CYCLING  
IN A NATURAL FOREST SETTING

A Thesis

Submitted to the Faculty

of

Purdue University

by

Grace Conyers

In Partial Fulfillment of the

Requirements for the Degree

of

Master of Science

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Purdue University

West Lafayette, Indiana

To the future.

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## ABSTRACT

Conyers, Grace. M.S, Purdue University, May, 2014. Cosmogenic beryllium cycling in a natural forest setting. Major Professor: Darryl Granger.

$^{10}\text{Be}_{\text{met}}$ , or cosmogenic beryllium, has a long half-life of 1.4 million years and quick adsorption on soil particles, which may make it ideal for dating soil erosion in historical context. However, there are questions on about the fundamental assumptions of the retentivity of  $^{10}\text{Be}_{\text{met}}$ . This manuscript explores these assumptions and the context of nutrient cycling in a natural forest setting.

To see if  $^{10}\text{Be}_{\text{met}}$  was being cycled through the trees, and at what rate, we looked at the [ $^{10}\text{Be}_{\text{met}}$ ] in the soil, 4 species of trees, and their leaves. The isotopic ratio  $^{10}\text{Be}/^9\text{Be}$  in all four tree species was comparable to the soil on which they grow, ranging from  $6\text{-}8 \times 10^{-9}$ . However, there was one exception with hickory (*Carya spp.*) which strongly bioaccumulate beryllium with an average of 0.38 ppm dry weight in the wood. Abscised hickory leaves have a higher [Be] of 2.0 ppm, over 10 times higher than in the soil.

Using standard allometric equations relating tree biomass to trunk diameter, and assuming that belowground biomass has the same [Be] as aboveground, we calculate that hickory trees at our site contain approximately 1% of the total  $^{10}\text{Be}_{\text{met}}$  under their canopy and that ~10% of this Be is cycled annually by leaf abscission. It is not clear at this point what fraction of litterfall Be is recycled into the plant, returned to the soil, or carried to groundwater as organic chelates.

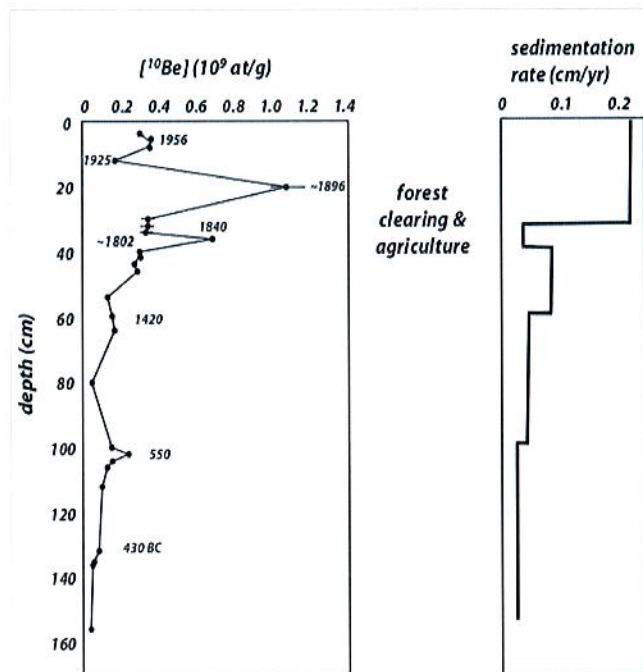
Hickory trees occupy an average of ~10% of the oak-hickory forest area. Assuming that trees are randomly distributed, that litterfall Be is returned to the soil, and maintaining a constant  $^{10}\text{Be}_{\text{met}}$  budget over time for simplicity, then more than half of all  $^{10}\text{Be}$  in the forest soil will have passed through a hickory tree over the past 10 ky. Fully 90% of all  $^{10}\text{Be}_{\text{met}}$  will pass through a hickory tree over a period of ~25 ky. It is clear that hickory trees can transport

a sizable fraction of the total  $^{10}\text{Be}_{\text{met}}$  in their nutrient cycle, and that they may be responsible for landscape-scale Be mobility.

## CHAPTER 1: INTRODUCTION

### 1.1 Overview of the problem

Soil is one of Earth's greatest resources. All terrestrial life ultimately depends on soil and water. It is used for food production for humans and animals alike, and it also supports the natural environment. This importance is reflected in the landscapes



*Illustration 1: The cosmogenic beryllium profile of Magothy River alludes to the idea that erosional history may be detected in offshore soil cores. Taken from Valette-Silver et al (1986).*

themselves. Where the ground is down to bare rock, there is neither much of plant nor animal life to speak of; yet life is teeming where there is a thick layer of healthy soil. Soil played a fundamental role in civilization's development. The Fertile Crescent could not have been as successful as it was without the richness of its soils. Without healthy soil, an agricultural civilization could not have flourished as it did. The rich soil provided a substrate in which crops could grow, feeding a quickly expanding and flourishing population.

The importance of the soil cannot be understated; thus, it is important to understand how the impacts of land use affect soil formation, soil degradation, and soil erosion rates. One way to interpret this information is through measuring soil erosion. While there are several ways this can be done, this manuscript focuses on the use of meteoric beryllium-10 ( $^{10}\text{Be}_{\text{met}}$ ) to measure soil erosion.  $^{10}\text{Be}_{\text{met}}$  is a radioactive isotope of beryllium that is produced in the upper atmosphere. It is a potentially ideal elemental tool to examine historical land use due its long half-life of 1.4 million years and quick adsorption on soil particles. However, questions about the fundamental assumptions of the retentivity of  $^{10}\text{Be}_{\text{met}}$  on the soil have surfaced.

Erosion studies using  $^{10}\text{Be}_{\text{met}}$  have been on going since the 1980s. If a simple “site inventory” method is used, which essentially assumes that all  $^{10}\text{Be}_{\text{met}}$  leaves the landscape via erosion, then soil erosion rates can be estimated from the flux of  $^{10}\text{Be}_{\text{met}}$  in river sediment (Brown, 1987). As shown by Willenbring and von Blanckenburg (2010), if the inventory of  $^{10}\text{Be}_{\text{met}}$  in the soil remains unchanged, then the erosion rate can be estimated from the concentration of  $^{10}\text{Be}_{\text{met}}$ , rather than its flux which is difficult to measure. If the concentration of  $^{10}\text{Be}_{\text{met}}$  in river sediment indicates the basin-wide erosion rate, one might think that  $^{10}\text{Be}_{\text{met}}$  in a sedimentary record could record the erosional impacts of historic land use. This means that sediments deposited in estuaries, bays, and lakes may be an indicator of the erosional history of the basin from which the sediments came. Valette-Silver et al. (1986) showed the potential for this method quite clearly when they analyzed three cores out of Chesapeake Bay and illustrated how there was a spike in [ $^{10}\text{Be}_{\text{met}}$ ] in the sediment which coincided with the deforestation and agricultural advancement of the Eastern United States in the late 18<sup>th</sup> and early 19<sup>th</sup> centuries (illus. 1).

One fundamental assumption of this method is that  $^{10}\text{Be}_{\text{met}}$  is tightly bound to soil particles. However, studies by Monaghan et al. (1983) and Pavich (1985) noted a loss of the  $^{10}\text{Be}_{\text{met}}$  to the soil inventory greater than predicted values. Losses are generally thought to be solutional losses (M.C. Monaghan et al., 1983) or due to chelation with organic materials prior to mobilization (M.J. Pavich et al., 1985). This contradicts previous assumptions of  $^{10}\text{Be}_{\text{met}}$  immobility commonly used in soil erosion studies.

Furthermore, living trees contain  $^{10}\text{Be}_{\text{met}}$  concentrations of  $10^6$  atoms/g (Klein, Middleton, & Tang, 1982).  $^{10}\text{Be}_{\text{met}}$  can also be present in high concentrations in decayed organic matter (Lundberg et al., 1983). Furthermore, there is experimental evidence that beryllium is mobilized in natural soils complexed with organic acids. For example, up to 50% of beryllium can be mobilized by humic acids in soils at pH 7 (Takahashi, Minai, Ambe, Makide, & Ambe, 1999). These observations were the foundation for the driving question for this study: what is the inventory and flux of  $^{10}\text{Be}_{\text{met}}$  in a natural forest setting? Is  $^{10}\text{Be}_{\text{met}}$  an immobile tracer of soil particles, or is it actively involved in vegetation cycling?

An understanding of soil formation and erosion will help elucidate the context and processes of deposition. In addition to natural processes, anthropogenic land use can further inform whether  $^{10}\text{Be}_{\text{met}}$  can be used to trace soil history. After describing these two facets of soil studies,  $^{10}\text{Be}_{\text{met}}$  itself will be discussed.

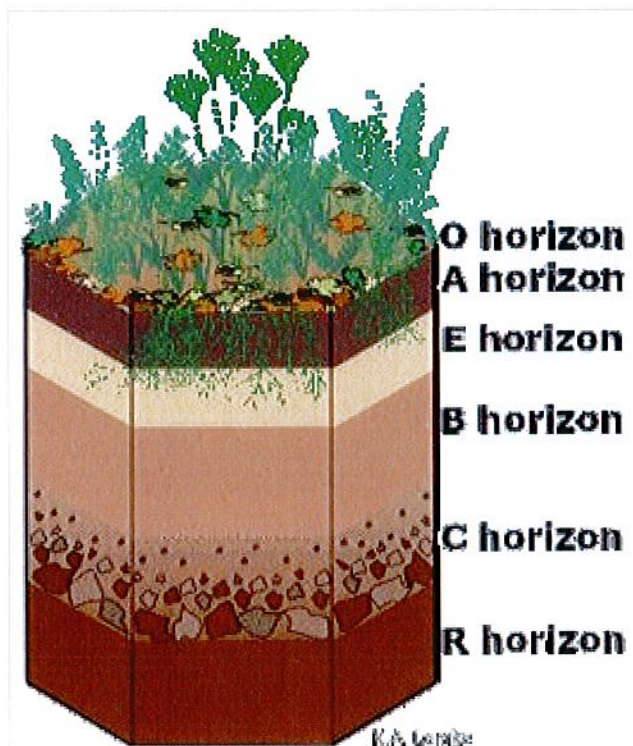
## 1.2 Soil Formation

Historically, civilization has exploded and thrived around fertile lands, yet we rarely give a second thought to the earth beneath our feet. Both the formation and erosion of soils are complex processes that are dependent on a wide variety of conditions. Jenny (1941) points out that soil formation is anything but simple, but it can be boiled down to five primary factors. These five factors are applicable to both soil formation and erosion. They are the parent material, topography, climate, vegetation and organisms, and time.

All soil is derived from a rock, known as the parent material. The nutrients that make up the soil come from minerals in the parent material. As different parent materials will produce different soils, each will have different nutrients. For example, granite will produce sandier soils, while a basalt might produce a soil with more clay. As the rocks weather, the minerals that once formed the rock are released as nutrients which local plants and animals capitalize on.

Topography describes the shape of the land. It contributes to the quantity and speed of soil erosion. Gentle sloping lands generally have thicker, more deeply weathered soils. The soils in this type of land have a slower turn-over rate, and thus may be older soils. In contrast, a steep sloping landscape will have thinner soils with freshly eroded nutrients available for the local biota. These soils have a faster turn over rate and are often relatively recently deposited.

Climate plays a role in how fast the nutrients are leached and cycled out of the soil. Hotter, humid climates leach the nutrients out of the soils. Most nutrients in these climates are cycled through the local flora and fauna. The soils in these climates tend to be thicker and older, but have fewer nutrients as they were leached out due to heavy



*Illustration 2: An ideal well-developed soil horizon has a 5 distinct layers with depth, including the regolith and parent material. Used with permission from Lemke (2010).*

precipitation. Cold climates, in contrast, are a frozen time capsule, and the rocks weather more slowly. The nutrients here are fresher, but vegetation has a harder time taking root, resulting in thinner soils.

The last major factor in soil formation and erosion is time. Over time, the previous factors alter the entire substrate and form distinct soil horizons. In the beginning, the rocks break down, the soils begins to form, and vegetation starts to take hold. How quickly this happens depends primarily on the climate, including temperature and precipitation. The



topography plays a secondary role in the soil formation as it dictates how well vegetation may take hold on the slopes or lack of slopes.

These five factors work together over time to create a unique soil at any given point in the landscape. Lemke's (2010) illustration (illus 2) shows how an ideal soil forms. The O horizon, at the very top of the soil column, is rich in organics. It is the layer most greatly influenced by the biota living in and off of the soil. The A horizon is the mineral horizon formed at or below the O horizon that contains an accumulation of decomposed organic matter. The E horizon is not always present; when it is, it is the zone where there is loss of silicate clay, Fe, and/or Al that leaves behind sand and silt particles. The B horizon is below the A, E, or O horizon, and is dominated by the obliteration of the original rock structure and the accumulation of silicate clay, Fe, and/or Al. The C horizon is described as the area being little affected by soil genesis. It is right above the R horizon and overlaps with the partially weathered rock. The R horizon is the hard, unweathered parent rock. This area encompasses the bedrock as well as the area of weathering just above it.

A very young soil is likely to have only the A and R horizons. As a soil ages, it forms the horizons described above, then gradually leaches away its A and B layers so there is a layer of biota at the top of a C horizon, which lies directly over highly weathered rock and the parent rock below.

A single landscape can have a variety of soils and a variety of soil formation rates. This is reflected poignantly in a catena. A soil catena is a sequence of different soil profiles that occur down a slope. They occur on hill slopes where the geology is uniform and there is no marked difference in climate from the top to the bottom of the slope. The variations in soil profile that occur down the slope are largely the result of changes in slope gradient. Soil can be eroded easily from a steep slope, but will tend to accumulate on shallower gradients. Soil water will drain freely on steep slopes, but will take much longer to drain from shallower ones. As permeability is reduced by soil accumulation, steep gradients encourage movement downslope rather than through the soil.

Consequently, many nutrients are washed downslope along with small particles. This has an effect on the texture and pH of the soil (Bird, 1957).

### 1.3 Soil Erosion

The opposite side of soil formation is soil erosion. Soil erosion is defined by the loosening, transportation, and deposition of soil. Soil erosion is a natural process that is responsible for the formation of fertile soils. These include alluvial valleys such as the Indus, Nile, Euphrates, and Yangtze and the loess soils of savannas such as the Loess Plateau of China and the United States' Great Plains and northwest region. There are many natural causes, or agents, of soil erosion. Wind, water, and gravity are constantly working on detaching the soils. Under equilibrium conditions, soil erodes at roughly the same rate it forms (Jenny, 1941); however, land use may be eroding this resource faster than it is formed (Montgomery, 2007b). Larger natural events such as violent storms, earthquakes, and volcanic eruptions cause dramatic and instant detachment of soil. Anthropogenic activities exacerbate the minor natural events, resulting in a much larger and dramatic shift in the record. In the context of quantifying erosion rates, faster erosion implies a younger soil. Conversely, slow erosion implies an older soil.

There are two causes of erosion: natural geological events such as changes affected by climate, earthquakes, and even biological activity of animals and anthropogenic, or the way humans affect the land. Impacts of these types of erosion can be obscure or obvious. The evidence for such impacts can be buried under layers of fresh soil, they can be fresh on the surface, or they can be blowing in the wind. It has been hypothesized that the evidence of soil degradation can be seen in human and animal migrations, in the change of vegetation (Vita-Finzi, 1969), or during political upheaval (Sinopoli & Morrison, 1995). There are subtle differences in soil erosion due to natural causes and anthropogenic causes. Accurately quantifying soil erosion rates is necessary in understanding the impacts of land use, both historic and modern (Montgomery, 2007a; Trimble & Crosson, 2000) and its impacts on soil formation rates (Jenny, 1941).

#### 1.4 Methods of measuring soil erosion rates and use analysis

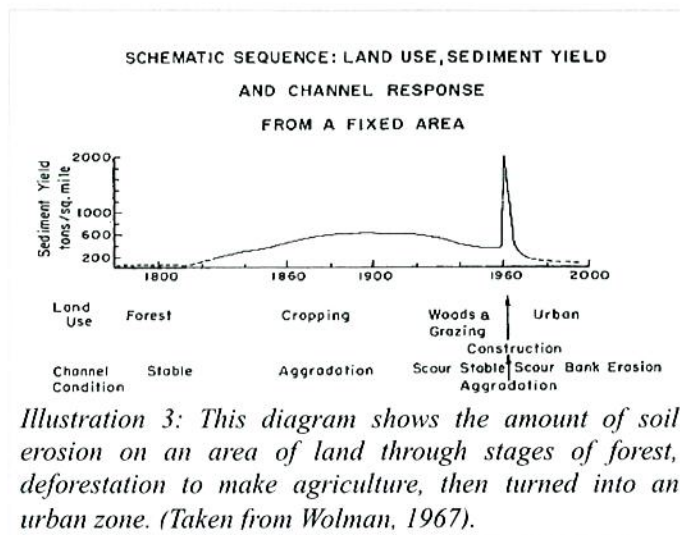
Accelerated soil erosion is a very destructive process that leads to adverse affects of long-term on-site productivity, siltation, and waterway pollution. Managing and controlling soil erosion have been around since the early days of agriculture, resulting in unique methods such as terracing. Despite this, modern analysis and quantification of soil erosion didn't come about until the American Dust Bowl of the 1930s. Even then, there were two foci of research prior to the 1980s: 1.) plot-watershed and plot only scales and 2.) erosional impact on soil quality and productivity. The major focus during the 20<sup>th</sup> century was on the rate of erosion and its impact on agricultural productivity and water quality (Rattan Lal, 2003).

##### 1.4.1 Quantifying short term soil erosion

Modern erosion rates have traditionally been measured with methods such as the universal soil loss equation (USLE), the revised universal soil loss equation (RUSLE), and the sediment delivery ratio (SDR). These methods predict approximate soil erosion given a certain set of conditions, which makes them useful for estimating the relative impacts of similar land uses. However, they do not estimate soil loss and redistribution for dissimilar land uses. For example, USLE and RUSLE can predict the long-term average annual rate of erosion on a field slope based on rainfall pattern, soil type, topography, crop system, and management practices. However, they only account for sheet or rill erosion, omitting gully, wind, and tillage erosion, and cannot account for a larger area than the single field slope. RUSLE is simply a revised and updated version of USLE, with improved maps and modified calculations – but it does not account for sediment deposited en route to the place of measurement, or gully and channel erosion downstream. (Singer & Munns, 2002).

To test the predictive models in any field, there must also be methods to check against reality. The sediment delivery ratio (SDR) is one of those methods. In essence, this is a dimensionless scaling factor used to account for differences in areally-averaged

sediment yields between measurement scales. SDR estimates and accounts for the amount of sediment that is actually transported from the eroding sources to the catchment outlet compared to the total amount of soil that is detached over the same area above that point (Hua Lu, Christopher Moran, Ian Prosser, & Murugesu Sivapalan, 2004). There is no precise procedure to estimate SDR, although the USDA has published a handbook in which the SDR is related to drainage area (USDA, 1972). This ratio varies widely with



size of area, steepness, density of drainage network, and many other factors. In order to estimate sediment delivery ratios, the size of the area of interest should also be defined.

In general, the larger the area size, the lower the SDR (Walling, 1983).

To study recent, short-term events there have been

successful studies of redistribution of soils in modern times using fallout radionuclides. These include  $^7\text{Be}$  (Matisoff, Bonniwell, & Whiting, 2000; Schuller et al., 2006), a short-lived cosmogenic nuclide ( $t_{1/2} = 52$  days) that is produced in the atmosphere and deposited primarily during rainfall. Cesium-137 ( $t_{1/2} = 30.17$  y) and  $^{210}\text{Pb}$  ( $t_{1/2} = 22$  y) were produced during atmospheric nuclear testing that peaked in the 1960s, and were deposited on soils at that time. These radionuclides are both particle-active, so their redistribution across the landscape reflects particle movement over decades (e.g., Matisoff et al., 2000). These radionuclides are useful for studying modern, short term events such as recent deforestation, a severe storm, or agriculture techniques.

The previous methods are used mostly to predict erosion given a certain set of conditions and to model them. They are used to quantify modern soil erosion rates, but not analyze the impact of historical land use on soil erosion. Wolman (1967) notes that

modernization is not necessarily to blame for dramatic scenes of erosion and environmental disasters. The lines of impact on soil erosion is blurred in modern day. Wolman (1967) shows that there are phases of a parcel of land goes through on it's way to being used for urbanization, each with its own amount of erosion (illus. 3). First, there is a forested land which has little erosion because it is held in place by vegetation. When the land is cleared to make agriculture, there is an increase of erosion to be expected. Agriculture itself has erosional episodes that lead to an elevated amount of sediment transport over time, especially when the fields are being tilled. After agricultural land is bought for development, there is a period where the ground lays fallow and shrubs are allowed to regrow, lowering the amount of sediment leaving the parcel of land for a time. Once construction starts, however, there is an immense spike in erosion for a short period until the construction is finished. Interestingly, after construction is finished, the amount of erosion and sediment transport tapers off and may dip to pre-agricultural levels.

#### 1.4.2 Quantifying Historic Land Use

There has been speculation that humans in ancient times caused a great deal of erosion and soil degradation which ultimately led to societal collapse around the world (Dale & Carter, 1955; Diamond, 2005; Hillel, 1991; Montgomery, 2007a). Evidence leading to this conclusion is often circumstantial, and usually based on records of sedimentation. For example, recent marine sediment records show that there was an intensification of soil weathering at approximately the same time as Iron Age Bantu-speaking farmers migrated across central Africa and grasslands began to proliferate (Bayon et al., 2012).

However, historical land use is difficult, if not impossible, to quantify with traditional methods. Instead, most commonly, the rate of reservoir sedimentation is taken as a proxy for erosion (Sheldon Judson & Ritter, 1964). Recently, this method was used to reexamine the erosional history of the Mayan Clays and correlate the sediment layers to changes in nearby cultures based on bits of artifacts, pollen, and carbon within the

layers (Carozza et al., 2007). Another way to measure soil erosion is to calculate the amount of soil that has been removed, leaving roots, foundations, rocks, and other stationary items exposed. For example, Jusdon (1963) measured erosion relative to archaeological horizons, such as foundations of Roman houses and cisterns. In this same area, Cyr et al. (2008) measured the geological erosion rates with  $^{10}\text{Be}$ , finding there was no reason to invoke rapid erosion due to land use.

This question of historical erosion rates can also be approached and answered using methods such as cosmogenic nuclides such as  $^{14}\text{C}$ , *in situ*  $^{10}\text{Be}$ , and others which can be found in rock grains (Cerling & Craig, 1994).  $^{14}\text{C}$  ( $t_{1/2} = 5,700$  y) is used to date organic material. Archaeologists often use this to date a sediment layer where the organic material was deposited (Renfrew & Bahn, 2004). The dates obtained, used in tandem with the depth of sediment above it, can measure approximate erosion rates. While  $^{14}\text{C}$  dating can accurately date things up to 50,000 years old, not all profiles will have a piece of carbon that can be dated.

$^{10}\text{Be}_{\text{met}}$ , a cosmogenic nuclide, adheres quickly to the soil particles, has a half-life of 1.4 Ma, and is abundant. This makes it ideal for measuring historical soil erosion. This particular aspect of  $^{10}\text{Be}_{\text{met}}$  is this manuscript's focus.  $^{10}\text{Be}_{\text{met}}$  is similar to the *in situ*  $^{10}\text{Be}$  in that it is produced via spallation. The two differ in that  $^{10}\text{Be}_{\text{met}}$  is produced in the atmosphere, whereas *in situ*  $^{10}\text{Be}$  is produced in the rocks themselves, particularly in quartz minerals.  $^{10}\text{Be}_{\text{met}}$  as a tool for dating soil erosion is advantageous because it is produced continually in the atmosphere, then, once it is on the soil, adheres to the soil particles and percolates downward. This gives it the potential to have a predictable and usable profile. However, to fully understand the usefulness of  $^{10}\text{Be}_{\text{met}}$ , its properties and limitations must be discussed. The next section will outline the properties of  $^{10}\text{Be}_{\text{met}}$ , and the section following that will discuss the research we did in more detail.

### 1.5 Properties of Meteoric beryllium-10 in the soil

Meteoric beryllium-10 is produced in the atmosphere via spallation of O<sub>2</sub> and N<sub>2</sub> (Lal & Peters, 1967). It adheres to dust particles within the troposphere, and circulates through the atmosphere for approximately a year until it falls to earth with dry or wet deposition (Raisbeck & Yiou, 1981). Once <sup>10</sup>Be<sub>met</sub> has reached the ground, it adheres quickly to soil particles. In the soil, <sup>10</sup>Be<sub>met</sub> is typically found distributed over the uppermost few decimeters to meters (Graly, Reusser, & Bierman, 2011), implying that it has some mobility in the soil profile. In all but very old or eroded soils, the <sup>10</sup>Be<sub>met</sub> concentration decreases at depth, suggesting that the inventory is retained within the soil column. It is thought, therefore, that <sup>10</sup>Be<sub>met</sub> is strongly adsorbed to soil particles. This behavior allows for <sup>10</sup>Be<sub>met</sub> to be used as a sediment erosion tracer.

#### 1.5.1 Retentivity in the soils

Beyond erosion, one needs to look at losses through solution and decay. Under most conditions, <sup>10</sup>Be<sub>met</sub> is tightly adsorbed onto the soil particles, and remains there. There are a few circumstances where meteoric beryllium is lost to the dissolved phase. These settings are identified and discussed below.

#### 1.5.2 Adsorption characteristics in soil

The soil adsorbs <sup>10</sup>Be<sub>met</sub> rapidly and holds onto it for long periods of time. Iron and aluminum are strong scavengers of beryllium.

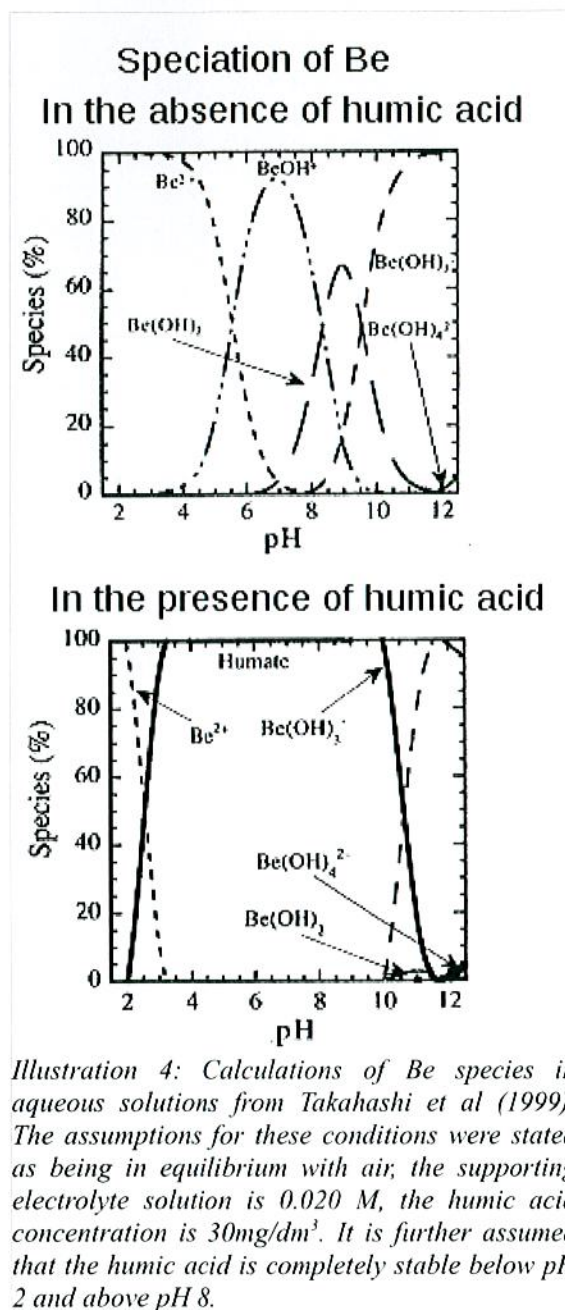
However, there are a few instances where <sup>10</sup>Be<sub>met</sub> is more mobile. For instance, redox systems have the ability to mobilize metals, including beryllium. This in turn increases the pH, which increases colloid development and dispersion (Sposito, 2008; Thompson, Chadwick, Boman, & Chorover, 2006). Where there are stable colloids, the

saprolite has a reduced capacity to retain metals, and beryllium is mobile (Kretzschmar, Robarge, & Amoozegar, 1995).

### 1.5.3 Speciation

In the absence of organic acids, most beryllium will be present above pH 5 as the hydrolyzed species. As hydroxides are very reactive, any dissolved  $^{10}\text{Be}_{\text{met}}$  is likely to be adsorbed onto clay minerals and Fe-rich hydroxides. Takahashi et al. (1999) calculated the dissolved species of beryllium in the presence and absence of humic acids at varying pH levels (illus. 4). This shows that in the absence of humic acid above pH 5, which is an acidic soil, beryllium is primarily found as the hydrolyzed species. However, in the presence of humic acid, beryllium can be expected to be in a humate complex in most normal soils.

The reactivity of an element can be quantified by measuring the ratio of concentrations of a compound adsorbed to a solid to the concentration in solution when the system is in equilibrium. This is called the partition coefficient ( $K_d$ ). At  $\text{pH} < 4$  the  $K_d$





is  $10^1$ , at pH 4 – 6, the  $K_d$  is  $10^2$  and  $10^5$  at pH >6 were observed for  $^7\text{Be}$  to be adsorbed from river water onto a variety of clays and mud within 7 days (You, Lee, & Li, 1989).

#### 1.5.4 Grain Size

Once  $^{10}\text{Be}_{\text{met}}$  is deposited on the soils, it adsorbs very quickly onto soil particles. Beryllium is insoluble except in acidic soils. Under basic conditions, beryllium may be adsorbed onto aluminosilicates, organic matter, or be precipitated with iron as a hydroxide. There is a larger surface area on smaller particles, thus, there will be more  $^{10}\text{Be}_{\text{met}}$  on the smaller clay particles than there will be in the same weight of the larger

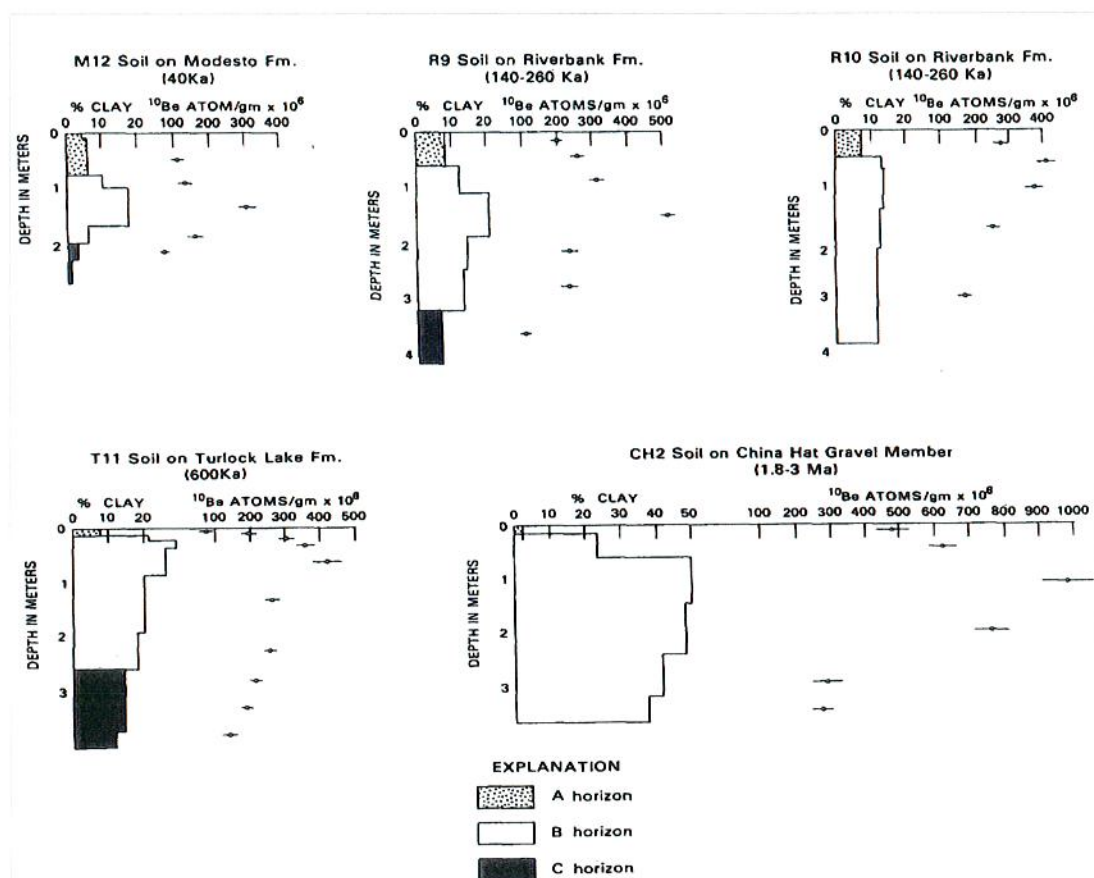


Illustration 5: Work from Pavich (1986) shows the ways that grain size and depth affect the soil profiles.

sand particles. This affects the concentration of  $^{10}\text{Be}_{\text{met}}$  in the soil profile (illus. 5), such that maximum amount of  $^{10}\text{Be}_{\text{met}}$  per gram of soil is where the clay content is the highest (Milan J. Pavich, Brown, Harden, Klein, & Middleton, 1986). To account for this,  $^{10}\text{Be}_{\text{met}}$  is normalized to another metal. Traditionally, this is done with iron (Heltz & Valette-Silver, 1992; van Green et al., 1999), but more recently it has been shown that  $^9\text{Be}$  provides much better normalization (Willenbring & von Blanckenburg, 2010).

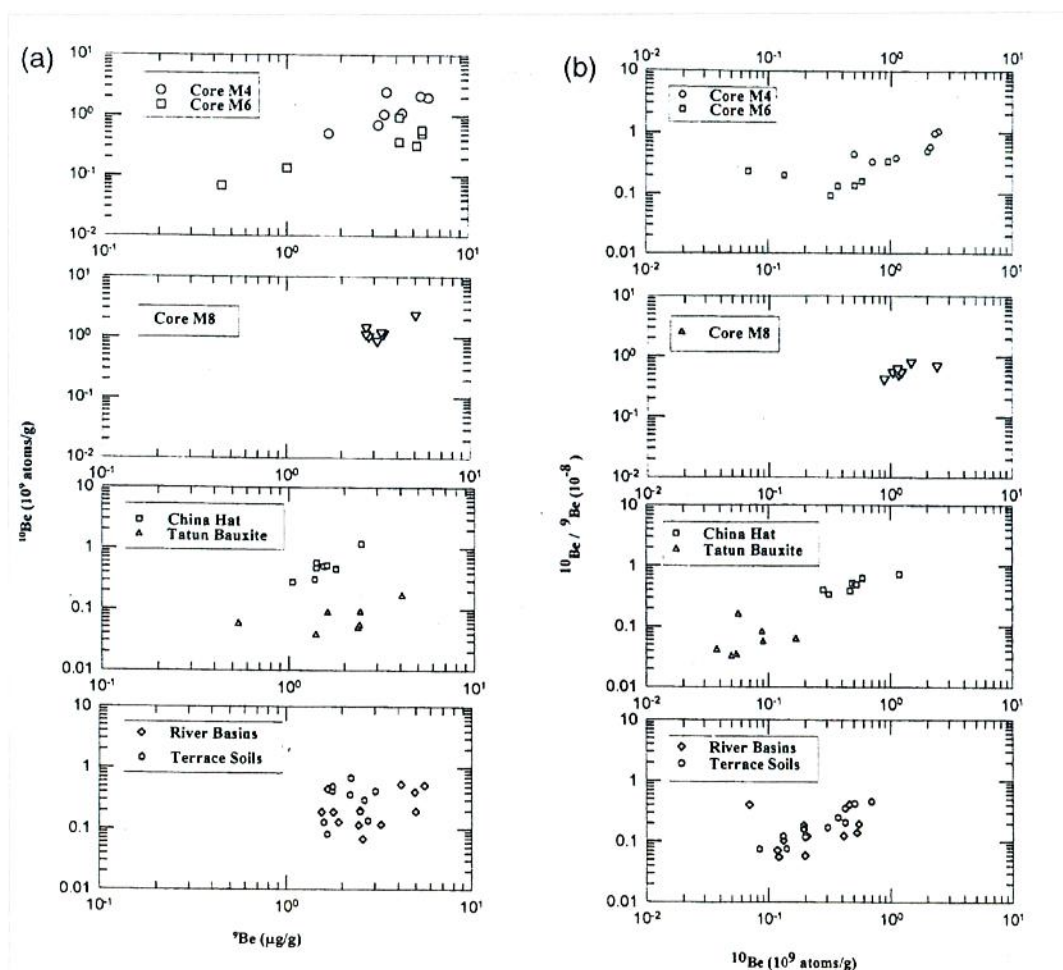


Illustration 6: Graphs from Barg et al, 1997 that illustrate the use of  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  ratios to date soil profiles.

## 1.6 Chronosequences

Chronosequences tell a story about the history of the soil, such as how long it's been forming or if there was a catastrophic erosion event.  $^{10}\text{Be}_{\text{met}}$  has a long half-life of 1.4 Ma and adheres quickly onto soil particles under a wide variety of conditions. It can be used to “fingerprint” recent erosion (Viparelli, Wesley Lauer, Belmont, & Parker, 2013) and long term erosion back to 8 Ma ((Willenbring & von Blanckenburg, 2010). Hence,  $^{10}\text{Be}_{\text{met}}$  can offer much insight into erosion across a great span of time.

As discussed in the introduction, we saw that if a simple “site inventory” method is used, which essentially assumes that all  $^{10}\text{Be}_{\text{met}}$  leaves the landscape via erosion, then soil erosion rates can be estimated from the flux of  $^{10}\text{Be}_{\text{met}}$  in river sediment (L. Brown, 1987). If the inventory of  $^{10}\text{Be}_{\text{met}}$  in the soil remains unchanged, then the erosion rate can be estimated from the concentration of  $^{10}\text{Be}_{\text{met}}$ , rather than its flux which is difficult to measure (Willenbring & von Blanckenburg, 2010). If the concentration of  $^{10}\text{Be}_{\text{met}}$  in river sediment indicates the basin-wide erosion rate, one might think that  $^{10}\text{Be}_{\text{met}}$  in a sedimentary records the chronosequence and within it, the erosional impacts of historic land use.

In cases where the measured inventory matches the predicted inventory, all the  $^{10}\text{Be}_{\text{met}}$  was retained. There are cases, however, where the measured inventory suggests a deficit. This apparent deficient is common in older soils where many of the exchange sites have been taken by other elements (E. T. Brown et al., 1992). There are other situations in which this may occur as well. These are when assigning an erosion rate of zero, when there is slow, steady erosion (Milan J. Pavich, Brown, Klein, & Middleton, 1984), a wrong independent age estimator is used, or when  $^{10}\text{Be}_{\text{met}}$  is lost or redistributed with solutions. These possibilities will be discussed in detail in Section 1.6.2.1.

### 1.6.1 Distribution

After  $^{10}\text{Be}_{\text{met}}$  adsorbs onto the soil particles, it would then move with the soil as it moves downward. In a soil where the grain sizes are homogeneous and there is no loss to

either solution or erosion, a soil profile will have a higher concentration of  $^{10}\text{Be}_{\text{met}}$  in the top few centimeters, and a steady decrease in  $[^{10}\text{Be}_{\text{met}}]$  as depth increases (illus. 5). As shown in Pavich (1986), this “ideal” profile can be altered by grain size distribution within the soil column, but that is accounted for with normalization to another metal, most often  $^9\text{Be}$ .

### 1.6.2 Watershed mass balances

$^{10}\text{Be}_{\text{met}}$  has been used as a passive tracer of sediment erosion in a watershed. There are two ways to think about this: an open system and a closed system. The beryllium fallout over the watershed has an average, which, if losses to erosion and solution are negligible and the soils are relatively young so as that the decay constant doesn't come into play, then what goes into the system should be able to indicate the age of the soil. This is the principle of the closed system. The open system assumes that there is some loss through erosion and solution, but that the natural decay of beryllium is negligible. We will first discuss the closed system model, then the open system model.

#### 1.6.2.1 Closed system

The simplified approach where the  $^{10}\text{Be}_{\text{met}}$  adsorbs onto the soil and leaves primarily due to erosion requires a closed system. If the system is closed, the  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  ratios and  $[^{10}\text{Be}_{\text{met}}]$  can be used as a dating method analogous to radiocarbon dating (Lal, Barg, & Pavich, 1991). A closed system requires a  $\text{pH} > 5$  in order to prevent the  $^{10}\text{Be}_{\text{met}}$  from being lost to solution and retained in mineral phases (although Graly et al. (2011) argue that Be is retained to significantly lower pH as an oxalate). Lal et al. (1991) describe a model with the potential to date soils based on the possible ratios of  $^9\text{Be}$  as it weathers in the soil profile and  $^{10}\text{Be}_{\text{met}}$  as it percolates down through the soil profile, allowing for the following formula:

$$[^{10}\text{Be}_{\text{met}}/^9\text{Be}] = \text{constant} \times [C(^{10}\text{Be}_{\text{met}})]^a \quad (1)$$

$$\text{where } \alpha = (\gamma - 1)/\gamma \quad (2)$$

In these formulae,  $C(^{10}\text{Be}_{\text{met}})$  is the concentration of  $^{10}\text{Be}_{\text{met}}$  in the soil core,  $\gamma$  is slope given by plotting  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  ratios (illus.6).

This model was tested over eight diverse soil profiles; the findings from the trials were that the highest  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  were at the bedrock as predicted (Barg, Lal, Pavich, Caffee, & Southon, 1997, illus. 6)). From these studies an age-depth model was suggested to be possible if acidic waters percolating through the soil were to be constant through time. If this is the case, then the  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  in the solution ( $R_0$ ) would have the following relationship to the authigenic mineral formed  $t$  years ago:

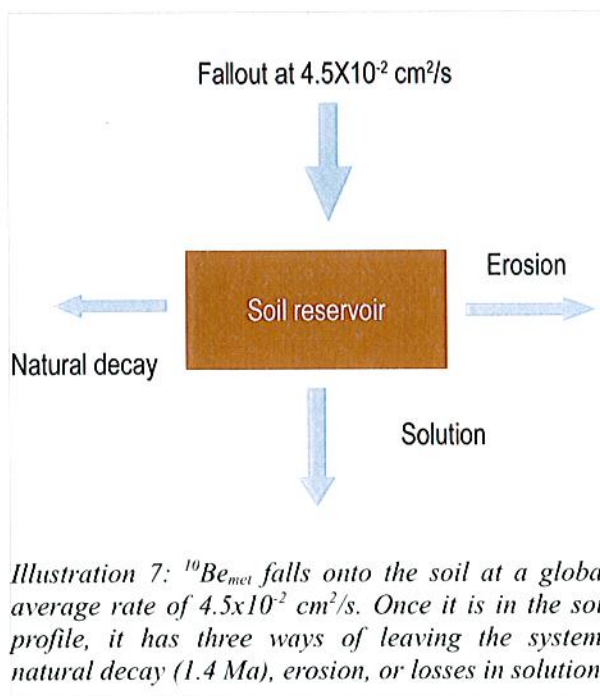
$$R(t) = R_0 e^{-\lambda t} \quad (3)$$

where  $\lambda$  is the decay constant for  $^{10}\text{Be}_{\text{met}}$ . Since depth is a function of time, this relationship can hold for a general case of uniform soil formation.

However, soils are not a closed system, and many assumptions need to be tested. With  $^{10}\text{Be}_{\text{met}}$  leached out of the soils at  $\text{pH} < 5$  (Takahashi et al., 1999), it is reasonable to ask if  $^{10}\text{Be}_{\text{met}}$  is quantitatively retained on soils. Furthermore,  $^{10}\text{Be}_{\text{met}}$  has been found in decayed organic material (Lundberg et al., 1983) and oak (Klein et al., 1982), while  $^9\text{Be}$  is found in a wide range of organic material (Grigor'yev, 1986a, 1986b).

#### 1.6.2.2 Open system

The long half life of  $^{10}\text{Be}_{\text{met}}$  ( $t_{1/2} = 1.4 \text{ Ma}$ ), its abundance, and its adherence to soil particles makes it a potentially good tracer for historical soil erosion. To understand how  $^{10}\text{Be}_{\text{met}}$  can be used to infer erosion



rates, it is useful to consider a simple model. Brown et al. (1988) noted that when  $^{10}\text{Be}_{\text{met}}$  is adsorbed onto the soils of an enclosed basin it has four ways to leave a basin: natural decay, loss in solution through surface run-off, loss through solution in ground water, and through soil erosion adsorbed onto soil particles (illus. 7). Although it is a simplified model, this provides the foundation of using  $^{10}\text{Be}_{\text{met}}$  for calculating soil erosion rates.

To illustrate this simple box model, start with the assumption that the fallout rate (F) is at the global average of  $\sim 10^6$  atoms/cm<sup>2</sup>/yr (Marc C. Monaghan, Krishnaswami, & Turekian, 1985; Willenbring & von Blanckenburg, 2010) and all the  $^{10}\text{Be}_{\text{met}}$  adsorbs onto the soil. Under steady-state conditions, in which the inventory of  $^{10}\text{Be}_{\text{met}}$  in the soil remains constant, the flux of  $^{10}\text{Be}_{\text{met}}$  out of the watershed (f) will be equal to the flux into the watershed. For a watershed of area A, and ignoring radioactive decay this corresponds to

$$f = FA \quad (4)$$

If the watershed has an erosion rate (E) of, say, 1 ton/ha/yr, and if all the  $^{10}\text{Be}$  leaving the watershed is adsorbed to soil particles, then the eroded sediment has a  $^{10}\text{Be}_{\text{met}}$  concentration of

$$[^{10}\text{Be}_{\text{met}}] = F/E = 10^8 \text{ at/g} \quad (5)$$

There are many assumptions in this model that will be violated under conditions of land use. Notably the system is not at steady-state. An increase in erosion rates should decrease the inventory of  $^{10}\text{Be}_{\text{met}}$ , which would theoretically lower the concentration of  $^{10}\text{Be}_{\text{met}}$  in the eroding sediment. Alternatively, land use might also result in a loss of  $^{10}\text{Be}_{\text{met}}$  from the watershed through a pathway that is not particulate erosion. For example,  $^{10}\text{Be}_{\text{met}}$  might be lost to groundwater or lost as particulate organic matter (POM) rather than as adsorbed to soil particles. This might cause the  $^{10}\text{Be}_{\text{met}}$  concentration in bulk sediment to rise, or the  $^{10}\text{Be}_{\text{met}}$  in the dissolved river load to rise. To understand which of these effects might be important, it is necessary to consider the factors that control  $^{10}\text{Be}_{\text{met}}$  retentivity in the soil.

There are two possible violations of this simple model that may be important in natural systems. First, if steady-state conditions are violated, e.g., by land use erosion,

climate change, or by vegetation change, then the export of  $^{10}\text{Be}_{\text{met}}$  out of the watershed will not be steady. For example, if there is a rapid increase in erosion, then there will be a spike in the  $^{10}\text{Be}_{\text{met}}$  concentration as surface soils are stripped, and then a longer-term dip associated with erosion of the deeper soil profile (Valette-Silver et al., 1986). A second complication is if there are significant losses of  $^{10}\text{Be}_{\text{met}}$  through mechanisms not anticipated in the simple model. For example, there may be losses of  $^{10}\text{Be}_{\text{met}}$  in solution that are facilitated by organic acids (Takahashi et al., 1999), there may be losses through organic matter (Lundberg et al., 1983), or there may be losses or gains to the watershed by aeolian transport.

### 1.7 $^{10}\text{Be}_{\text{met}}$ in plant litter and sediment rich in organic carbon

As meteoric cosmogenic  $^{10}\text{Be}$  is increasingly used to determine erosion and soil transport rates, it is important to consider their role in organic complexes and their behaviour in the organic part of the geochemical cycle. As noted earlier, there is experimental evidence that beryllium is mobilized in natural soils complexed with organic acids. For example, up to 50% of beryllium can be mobilized by humic acids in soils at pH 7 (Takahashi et al., 1999). Beryllium is also known to be taken up in plants such as tobacco and vegetables (“Environmental Health Criteria 106: Beryllium,” 1990; Grigor’yev, 1986a, 1986b) at ppm levels, primarily as organic acid chelates. It is not known to what extent biological beryllium transport in the environment affects the cosmogenic  $^{10}\text{Be}$  budget, or how it influences beryllium mobility.

It has been observed that decayed organic matter in soils and sediments contains very high concentrations of  $^{10}\text{Be}$  of up to  $10^9$ - $10^{10}$  atoms/g (Lundberg et al., 1983). On the other hand, living trees contain much lower concentrations of  $10^6$  atoms/g (Klein et al., 1982). The driving questions for this study, then, are 1.) what are the transfer factors for  $^{10}\text{Be}_{\text{met}}$  in a natural forest setting and 2.) does fungi play significant role in sequestering  $^{10}\text{Be}_{\text{met}}$ ?

### 1.7.1 Meteoric beryllium-10 uptake to the biosphere

Here we narrow down on the role of the biosphere, and speculate on how it might affect the  $^{10}\text{Be}_{\text{met}}$  geochemical cycle. The uptake into the biosphere is currently not well understood, and must be quantified to be able to gain a full understanding of  $^{10}\text{Be}_{\text{met}}$  system. This manuscript looks at two different ways that  $^{10}\text{Be}_{\text{met}}$  may be taken up into the biosphere: roots from trees (ch. 2) and fungus (ch.3).



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## CHAPTER 2: INVENTORY IN WOOD, LEAVES, AND NUTS

### 2.1 Introduction

This chapter focuses on estimating the beryllium isotopic inventory and the rate of beryllium isotopic cycling within a forest ecosystem. As discussed in the previous chapter, meteoric  $^{10}\text{Be}$  has been widely used for studying soil formation and erosion processes. Measurements of  $^{10}\text{Be}_{\text{met}}$  inventories in soils are commonplace and are a long-established procedure for estimating soil ages. However,  $^{10}\text{Be}_{\text{met}}$  has not been inventoried within a forest biomass, nor has the flux of  $^{10}\text{Be}_{\text{met}}$  through the living system been explored, much less quantified.

Balancing elemental cycles is a process that is similar to accounting. The process accounts for nutrients coming into the system with those leaving over a fixed amount of time. Balancing techniques are not standardized, so comparison among studies can be difficult

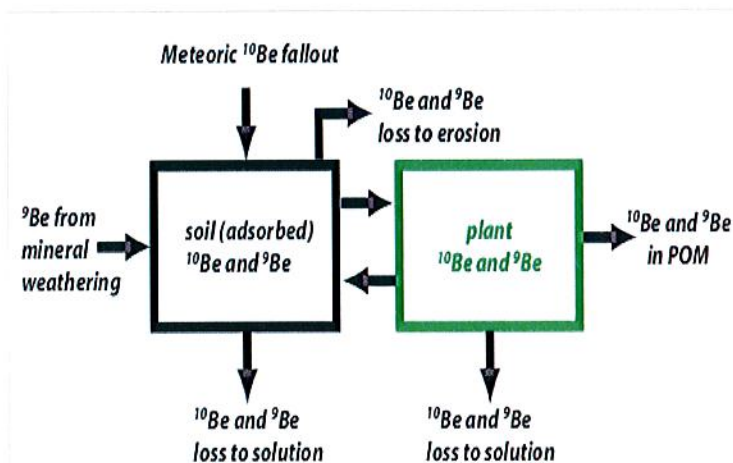


Illustration 8: This diagram shows the possible biogeochemical avenues for  $^9\text{Be}$  and  $^{10}\text{Be}_{\text{met}}$  to take through a living system.



(Wander, 2011). Because of this, we took the simplest approach to defining the system and calculating the inventory and balance as explained below.

This starts with Brown's (1988) premise that  $^{10}\text{Be}_{\text{met}}$  has 4 primary ways of leaving the system as discussed in chapter 1, section 1.5.2.2. The  $^{10}\text{Be}_{\text{met}}$  can leave the soil by leaching into the ground water, cycling into the biosphere, erosion, and/or natural decay. In the scenario described by Brown (1988), natural decay is negligible and the role of the biosphere is ignored. This study begins an exploration into the role of the biosphere in the geochemical cycle of cosmogenic beryllium-10.

To simplify the study the role of  $^{10}\text{Be}_{\text{met}}$  in the biosphere, I chose an area for my study site that is glacial till, providing a young soil with negligible natural decay. The study site also has a minimal amount of erosional features, which ensures that soil erosion can also be ignored. We further assume that surface run-off is negligible because of the well draining soils and fairly even topography, leaving the only potential for solutional loss to be via leaching into ground water. The potential for this is considered with the acidity of the soils, as discussed in chapter 1, section 1.5.3.

With this in mind, we can consider illustration 8, showing simplified possibilities of biogeochemical avenues that  $^{10}\text{Be}_{\text{met}}$  might take through the biogeochemical cycle. As we know,  $^{10}\text{Be}_{\text{met}}$  is distributed by dry and wet deposition. Once it falls to the ground, it is integrated into the soil. The portion that stays on vegetation and other surfaces is very little, and thus is negligible for the purpose of this study. The  $^{10}\text{Be}_{\text{met}}$  can then either be lost to solution or taken up into vegetation. In this study we focus on the uptake into vegetation, and more specifically, four tree species that are commonplace in the natural forest setting.

As the tree takes up nutrients from the soil,  $^{10}\text{Be}_{\text{met}}$  goes with it, where it can accumulate in the tree or travel up through the branches and into the leaves, nuts and flowers. Throughout the spring and summer, the tree uses available nutrients to grow. In the fall, any unnecessary nutrients the tree doesn't need for overwintering are pushed to the leaves, and thus lost at leaf fall. The nutrients that were harbored in the leaves are

released back into the soils during decay. These nutrients can then be recycled into the trees or lost to solution.

There are two different ways that inventory studies of this system could be done. One is to focus on a single tree, the soil beneath it, and the leaves that it sheds. This approach would be best for understanding the processes that are active within a specific tree, but might be subject to physiological differences of individual trees or locations. Another approach is to collect from multiple trees and to average the material together, treating it as representative of the forest population. This approach is more general, and averages over the variability that might be present in any particular tree. The averaging approach is not good for exploring details such as  $^{10}\text{Be}$  uptake as a function of tree location or tree age, but it is good for exploring broad differences among various species. I chose to use the more general approach since so little is known about Be cycling.

### 2.1.1 Flux of meteoric beryllium through trees

Plants get their nutrients from the soil as they are absorbed through the roots and taken up into the plant. In a deciduous forest, trees will push unused and unneeded nutrients through to the leaves, where they will be shed annually. These leaves decay and the nutrients are redistributed to the soil. This turnover rate is modeled by the flux through the tree. To first order, the flux of Be through a deciduous tree will be determined by its average concentration in the leaves ( $[\text{Be}]_{\text{leaf}}$ ) multiplied by the annual leaf fall ( $F_{\text{leaf}}$ ). Woody litterfall accounts for 20-25% of the total litterfall; its contribution to beryllium cycling can be calculated separately, but is ignored in this derivation for clarity.

$$F_{\text{Be}} = [\text{Be}]_{\text{leaf}} F_{\text{leaf}} \quad (1)$$

The flux of  $^{10}\text{Be}$  will be proportional to the total Be flux multiplied by the isotopic ratio of  $^{10}\text{Be}/^9\text{Be}$  in the leaf, here denoted by  $R_{\text{leaf}}$ .

$$F_{^{10}\text{Be}} = R_{\text{leaf}} [\text{Be}]_{\text{leaf}} F_{\text{leaf}} \quad (2)$$

The Be isotopic ratio within the leaves ( $R_{\text{leaf}}$ ) depends on several factors. Meteoric  $^{10}\text{Be}$  is available to tree roots from an exchangeable reservoir that is ultimately derived

from atmospheric input.  $^9\text{Be}$  may also be available from the exchangeable reservoir, but is also available from a primary mineral source. The relative amounts of  $^{10}\text{Be}$  and  $^9\text{Be}$  taken into the tree and its leaves will depend on the availability of the two isotopes within the soil as well as the depth distribution of the tree roots.

We assume that both  $^{10}\text{Be}$  and  $^9\text{Be}$  are taken into the roots at a rate that is proportional to their concentrations and to the abundance of roots. The distribution of roots within various ecosystems is well studied. According to the review of Jackson et al. (R. B. Jackson et al., 1996), the cumulative distribution of roots in a deciduous forest is given by,

$$Y = 1 - \beta^x \quad (3)$$

where  $x$  is depth in cm, and  $\beta$  is an empirical factor, which is equal to 0.966 (R. B. Jackson et al., 1996). As noted earlier,  $^{10}\text{Be}_{\text{met}}$  percolates down through the soil column over time. Thus, to estimate how much  $^{10}\text{Be}_{\text{met}}$  is taken up by the trees, we need to find the frequency of roots at depth (cm) from the surface. To get the frequency of the roots as a function of depth, we differentiate, giving the following:

$$\delta Y / \delta x = (-\ln \beta) \beta^x \text{ roots/cm} \quad (4)$$

The likelihood of any  $^{10}\text{Be}_{\text{met}}$  atom within the soil being taken up by the tree should be proportional to the number of roots in the same soil parcel. A dimensionless weighting factor,  $W(x)$ , which is proportional to the number of roots can be written:

$$W(x) = \beta^{x/x_0} = e^{-mx} \quad (5)$$

where  $m$  is an attenuation coefficient.

$$m = -x_0 / \ln \beta \quad (6)$$

For a deciduous forest with  $\beta = 0.966$  the attenuation length ( $1/m$ ) is approximately 30 cm.

To predict the relative amounts of  $^{10}\text{Be}$  and  $^9\text{Be}$  in the leaves, we need to multiply the root abundance weighting factor by the amount of available  $^{10}\text{Be}$  and  $^9\text{Be}$ .

We begin by calculating the uptake of  $^{10}\text{Be}$  into the leaves. For ease of calculation we assume that the meteoric  $^{10}\text{Be}$  decreases exponentially with depth ( $x$ ). The exponential approximation is a simplification, but reflects the common observation that meteoric  $^{10}\text{Be}$

is highest near the surface. Typical e-folding lengths ( $1/k$ ) for meteoric  $^{10}\text{Be}$  range from 5-50 cm (e.g., (Willenbring & von Blanckenburg, 2010).

$$[^{10}\text{Be}]_{\text{soil}} = [^{10}\text{Be}]_{\text{surf}} e^{-kx} \quad (7)$$

The weighted integral of the available  $^{10}\text{Be}$  should yield the relative amount of  $^{10}\text{Be}$  taken into the tree and its leaves.

$$[^{10}\text{Be}]_{\text{leaf}} = \int [^{10}\text{Be}]_{\text{soil}} W(x) dx / \int W(x) dx \quad (8)$$

$$[^{10}\text{Be}]_{\text{leaf}} = \int [^{10}\text{Be}]_{\text{surf}} e^{-kx} e^{-mx} dx / \int e^{-mx} dx \quad (9)$$

Evaluating from 0 to  $\infty$  yields

$$[^{10}\text{Be}]_{\text{leaf}} = [^{10}\text{Be}]_{\text{surf}} m (k+m)^{-1} \quad (10)$$

A similar calculation can be made for  $^9\text{Be}$  in both the exchangeable and the mineral reservoirs. However, since it is difficult to know a priori how the  $^9\text{Be}$  concentration in the exchangeable reservoir varies with depth, two endmember cases can be considered. In the first (model A), Be is largely immobile within the soil, and the exchangeable reservoir simply reflects local mineral weathering. In this case, the  $^9\text{Be}$  concentration will be uniform with depth.

$$[^9\text{Be}]_{\text{exch}} = \text{constant} \quad (11)$$

The relative amount of  $^9\text{Be}$  in the leaf is then simply proportional to the amount of exchangeable  $^9\text{Be}$ .

$$[^9\text{Be}]_{\text{leaf,exch}} = [^9\text{Be}]_{\text{exch}} \quad (12)$$

In the second endmember case (model B), beryllium is highly mobile in the soil and its profile reflects primarily chemical and biological turnover rather than in situ weathering. This scenario was envisioned by Grigor'yev (1986a, 1986b), who observed that beryllium tends to be concentrated near the surface, and suggested that 'beryllium is highly mobile...' In this case, one might expect the  $^9\text{Be}$  concentration in the exchangeable fraction to follow the  $^{10}\text{Be}$  profile.

$$[^9\text{Be}]_{\text{exch}} = [^9\text{Be}]_{\text{surf}} e^{-kx} \quad (13)$$

In this case, the relative amount of  $^9\text{Be}$  taken into the leaf should be proportional to the amount of  $^{10}\text{Be}$ , following equation (14).

$$[^9\text{Be}]_{\text{leaf,exch}} = [^9\text{Be}]_{\text{surf}} m (k+m)^{-1} \quad (14)$$

Finally, we need to estimate the amount of Be taken into the leaf from mineral weathering. Because  $^{10}\text{Be}$  is generally not available from mineral weathering, this pool only contributes to  $^9\text{Be}$  and serves to dilute the  $^{10}\text{Be}/^9\text{Be}$  ratio.

$$R_{\text{leaf}} = f_{\text{exch}} [^{10}\text{Be}]_{\text{leaf}} \{(1-f_{\text{exch}})[\text{Be}]_{\text{mineral}} + f_{\text{exch}} [\text{Be}]_{\text{leaf,exch}}\}^{-1} \quad (15)$$

For the case of relatively immobile  $^9\text{Be}$  with a uniform vertical profile

$$R_{\text{leaf}} = f_{\text{exch}} [^{10}\text{Be}]_{\text{surf}} m (k+m)^{-1} \{[\text{Be}]_{\text{exch}}\}^{-1} \quad (16)$$

For the case of relatively mobile  $^9\text{Be}$  with a profile that follows  $^{10}\text{Be}$

$$R_{\text{leaf}} = f_{\text{exch}} [^{10}\text{Be}]_{\text{surf}} / [\text{Be}]_{\text{surf}} \quad (17)$$

Which equation to use, 16 or 17 will depend on field measurements. If  $[^9\text{Be}]_{\text{exch}}$  is uniform then this indicates that beryllium is relatively immobile. On the other hand, if measured  $^{10}\text{Be}/^9\text{Be}$  ratios within the exchangeable fraction are constant over the rooting depth, then this is strong evidence that beryllium is being mobilized and isotopically homogenized by biogeochemical cycling. The fraction of beryllium from the exchangeable pool of the soil can be estimated in both cases using the appropriate equation.

The annual flux of  $^{10}\text{Be}$  through a tree is therefore given by substitution of (16) into (2). For relatively immobile Be, this yields

$$F_{^{10}\text{Be}} = f_{\text{exch}} [^{10}\text{Be}]_{\text{surf}} m (k+m)^{-1} \{[\text{Be}]_{\text{leaf}} / [\text{Be}]_{\text{exch}}\} F_{\text{leaf}} \quad (18)$$

For relatively mobile Be, equation 17 yields

$$F_{^{10}\text{Be}} = f_{\text{exch}} [^{10}\text{Be}]_{\text{surf}} \{[\text{Be}]_{\text{leaf}} / [\text{Be}]_{\text{surf}}\} F_{\text{leaf}} \quad (19)$$

The turnover time of  $^{10}\text{Be}$  within the soil can then be estimated by dividing the total inventory of  $^{10}\text{Be}$  by the flux of  $^{10}\text{Be}$  through the trees. Given the approximation of an exponential decrease in  $^{10}\text{Be}$  with depth (equation 5), the total inventory  $I$  per unit area of soil  $A$  can be solved analytically.

$$I = \int [^{10}\text{Be}]_{\text{surf}} \rho_{\text{soil}} A e^{-kx} dx \quad (20)$$

$$I = [^{10}\text{Be}]_{\text{surf}} \rho_{\text{soil}} A k^{-1} \quad (21)$$

The turnover time  $\tau$  is then obtained by dividing equation (21) by equation (18).

For relatively immobile beryllium, the turnover time is given by

$$\tau = \rho_{\text{soil}} A k^{-1} \{f_{\text{exch}} m (k+m)^{-1} \{[\text{Be}]_{\text{leaf}} / [\text{Be}]_{\text{exch}}\} F_{\text{leaf}}\}^{-1} \quad (22)$$

The ratio of beryllium in the leaves to that in the exchangeable pool of the soil can be referred to as a transfer factor  $T_{\text{leaf}}$ . Using this notation for the case of immobile beryllium leads to:

$$\tau = T_{\text{leaf}}^{-1} (F_{\text{leaf}}/A)^{-1} \rho_{\text{soil}} (1/m + 1/k) f^{-1} \quad (23)$$

The turnover time for relatively mobile beryllium is given by

$$\tau = \rho_{\text{soil}} A k^{-1} \{ f_{\text{exch}} \{ [\text{Be}]_{\text{leaf}} / [\text{Be}]_{\text{surf}} \} F_{\text{leaf}} \}^{-1} \quad (24)$$

$$\tau = \rho_{\text{soil}} T_{\text{leaf}}^{-1} (F_{\text{leaf}}/A)^{-1} f^{-1} k^{-1} \quad (25)$$

The turnover time of  $^{10}\text{Be}$  in a deciduous forest can therefore be determined from simple measurements of the Be enrichment factor  $E_{\text{leaf}}$ , the annual leaf fall per unit area, and the relative penetration lengths of roots and  $^{10}\text{Be}$ , together with physical parameters such as the density of soil. Contributions from woody litterfall can be calculated using the same equations, but by replacing the enrichment factor for leaves with a separate enrichment factor for wood ( $T_{\text{wood}} = [\text{Be}]_{\text{wood}} / [\text{Be}]_{\text{soil}}$ ). Interestingly, the turnover time is independent of the  $^{10}\text{Be}$  concentration in the soil.

Typical values for the parameters in equation (23) are:

$$1/m = 30 \text{ cm}$$

$$1/k = 5\text{-}50 \text{ cm (in alkaline soils)}$$

$$F_{\text{leaf}} = 0.03\text{-}0.04 \text{ g cm}^{-2} \text{ yr}^{-1}$$

$$\rho_{\text{soil}} = 1.5 \text{ g cm}^{-3}$$

To determine turnover times of  $^{10}\text{Be}$  in a natural forest, we determined beryllium transfer factors from analyses of soil and leaves and nuts from three species of tree in a 1 ha experimental forest plot in north-central Indiana, USA.

Our system is a mature forest on a one hectare plot in Martell Experimental Forest. Martell was chosen for its well characterised soils, history, representative tree species showing full progression and its reasonable size. To establish a basic inventory, we estimate the average beryllium concentrations and isotopic ratios in the soil and in tree stems (separated by dominant species). Then, to estimate the annual cycling of beryllium through the biologic system, we determined the average beryllium content and isotopic ratios in abscised leaves (again separated by dominant tree species), and use this

in combination with estimates of annual leaf litter generation to determine the approximate flux of  $^{10}\text{Be}_{\text{met}}$  and  $^9\text{Be}$ .

## 2.2 Martell Forest

Forest is an experimental forest owned by Purdue University. It is in the Central Till Plain in Tippecanoe County, Indiana, 8.5 miles from the Purdue University West Lafayette campus, south of State Road 26. The property is situated along the valley of Indian Creek, a tributary to the Wabash River and contains a total of 424 acres with 370 acres of forest. While Indian Creek is deeply incised, the forest property includes a wide alluviated valley bottom, steep slopes cut into glacial till, and an upper till plain that is variably mantled with loess.

My field site is approximately 1 ha located on the upper till plain in the northern segment of Martell Forest (illus. 9, appendix A). The plot is located approximately 10 meters off a gravel road maintained by the Martell staff. A tributary of Indian Creek runs north-south about 300 meters to



*Illustration 9: Aerial photos of Martell Forest dating back to 1938. My field site is denoted by the red box.*

the west of plot; 30 meters to the north of the plot is a smaller ravine that is becoming filled in by undergrowth. The hectare plot has low relief, but drains north and west towards the narrow ravines. The hectare plot is highest in the middle, with a small swale filled with undergrowth that cuts 20 meters into the northern boundary of the site. The site was chosen intentionally to have minimal relief and as uniform a soil as possible.

There has been no formal management of the forest containing my small plot since it was purchased in 1975 for Martell forest. A previous report (Meier, 2010) stated that there is evidence of small scale timber stand improvement in some areas in the 1980's and 90's, but did not state specifically where. Historic aerial photos (figure 9) show that it was a mature forest as early as 1938.

The soils of this site are classified as Strawn-Rodman (SyF) and Rainsville silt loam (RaB2) (Meier, 2010; USDA, 2012). Both types of soil are similar, but just slightly different from one another. The SyF series is described as being a loamy till to a loamy outwash over sandy and gravelly outwash, noted for woody vegetation. Its maximum  $\text{CaCO}_3$  levels are between 40 – 55%. The

RaB2 is described as being a loess over loamy outwash over loamy till. Similarly, the maximum  $\text{CaCO}_3$  is 40%. At my site, the soils were a silty loam over glacial till. The soil pH averaged around 5 for each of 10 soil cores, indicating a low  $\text{CaCO}_3$  content (see pH section, table 2).

The predominant tree species within the plot are black oak, white oak, and maple. Yellow poplar was common in the recent past (Meier, personal communication), but at the time of this study it was not as common as some of the other trees. There are also a significant amount of sugar maples and red hickories. These hickories are mostly in the southern half of the site, while the maples are scattered throughout. To a lesser degree, there are several black cherries and slippery elms in the northern half of the site.

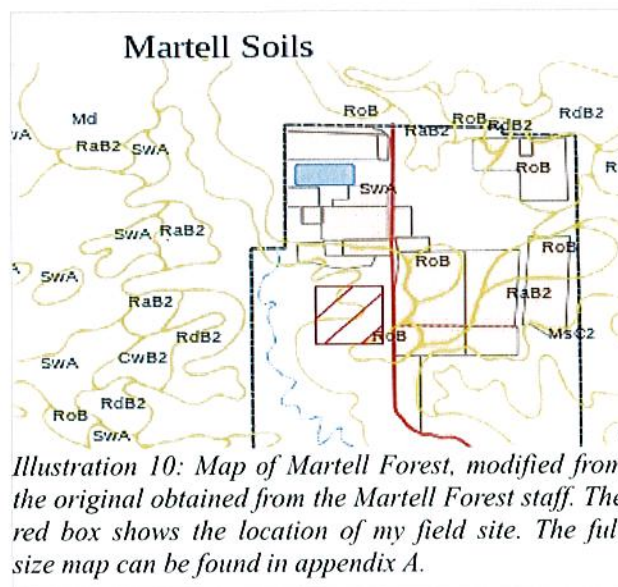


Illustration 10: Map of Martell Forest, modified from the original obtained from the Martell Forest staff. The red box shows the location of my field site. The full size map can be found in appendix A.



### 2.2.1 Site survey

To better characterize my hectare plot, and to quantitatively budget the  $^{10}\text{Be}_{\text{met}}$  within it, I performed a detailed survey of all standing trees (>15 cm diameter at breast height or DBH), and also analyzed 10 soil cores distributed across the site. Leaves from 4 species of trees, two from early successional, tulip and maple, and two from late successional with oak and hickory. Nuts were also collected to analyze throughput of nutrients.

#### Trees

The boundaries of the site were measured with tape and compass. Within the hectare plot each standing live tree was surveyed using a compass and laser distance measurer (Bosch GLR225) and plotted on a planetable. Most trees were surveyed from

	DBH of trees		
	Lowest	Highest	Average
Hickory	4.6	52.8	19.7
Maple	3.2	23.2	11.4
Oak	9.6	84.7	40.3
Tulip	6.4	102.6	35.9

*Table 1: The highest, lowest, and average DBH are shown in centimeters. The DBH was calculated using the circumference of the tree measured approximate 1.4 m off the ground.*

multiple locations within the plot to ensure survey accuracy by triangulation. Survey errors are estimated to be less than a few decimeters, comparable to the diameters of the trees.

Each tree was identified to species level by leaf, bark and, when possible, fruit or nuts, using a tree identification book (M.

T. Jackson, 2004). The circumference of each tree was measured by tape at 1.4 m above the ground; these numbers were used to calculate diameter at breast height (DBH) (See Appendix I and table 1). Diameters of the trees range from 3.2 cm in the maples to 102.6 cm tulips (table 1). The oaks and tulip trees are often the biggest trees in the hectare, while hickories and maples are smaller. The black cherries, which have a medium diameter, and slippery elms, which are about the same size diameters as maples, were not tested for beryllium content, so DBH of individual trees were not collected for every tree.

### Soils

Soils were previously surveyed, and a detailed soil map is available through Natural Resources Conservation Service (NRCS) website. This map (illus. 10) shows that there are two very similar soil types within my 1 ha plot. Using this map as well as the survey of the trees, locations for soil samples that would serve for soil analysis was based on a fairly even distribution through the plot making sure to gather samples from both soil types and the varying topography. At each of 10 sites, a core was taken using a bucket auger to a depth of 1 m, and soil texture and pH were noted for each 10 cm interval. An aliquot from each core was combined into an amalgamated sample to determine the average beryllium concentrations and  $^{10}\text{Be}/^9\text{Be}$  ratios at depths of 0-10 cm, 10-20 cm, 40-50 cm, and 90-100 cm.

Soils from each core were similar, consisting of a silty loam near the surface, grading to a more compact clay-rich till at the bottom. Carbonate contents

were negligible and pH was uniformly low, ranging from 4.8-5.5 (Table 2).

Core A	pH	Core B	pH	Core C	pH
0 - 10	5.3	0 - 10	4.8	0 - 10	5.0
10 - 20	5.3	10 - 20	5.3	10 - 20	4.8
40 - 50	5.0	40 - 50	4.8	40 - 50	4.8
90 - 100	4.5	90 - 100	4.8	90 - 100	4.8
Core D	pH	Core E	pH	Core F	pH
0 - 10	5.0	0 - 10	5.3	0 - 10	5.5
10 - 20	5.3	10 - 20	5.3	10 - 20	5.3
40 - 50	4.8	40 - 50	4.8	40 - 50	5.0
90 - 100	4.8	90 - 100	4.8	90 - 100	5.3
Core G	pH	Core H	pH	Core I	pH
0 - 10	5.3	0 - 10	5.0	0 - 10	4.8
10 - 20	5.3	10 - 20	4.8	10 - 20	4.8
40 - 50	5.0	40 - 50	5.0	40 - 50	4.8
90 - 100	5.0	90 - 100	5.0	90 - 100	5.3
Core J	pH	Combined cores	pH		
0 - 10	4.8	0 - 10	5.0		
10 - 20	4.8	10 - 20	4.8		
40 - 50	4.8	40 - 50	4.8		
90 - 100	5.0	90 - 100	5.0		

*Table 2: Soil cores taken randomly throughout the site were broken into 10cm increments, and the pH of each increment was taken individually. All of the soils were between pH 4.8 and 5.3.*

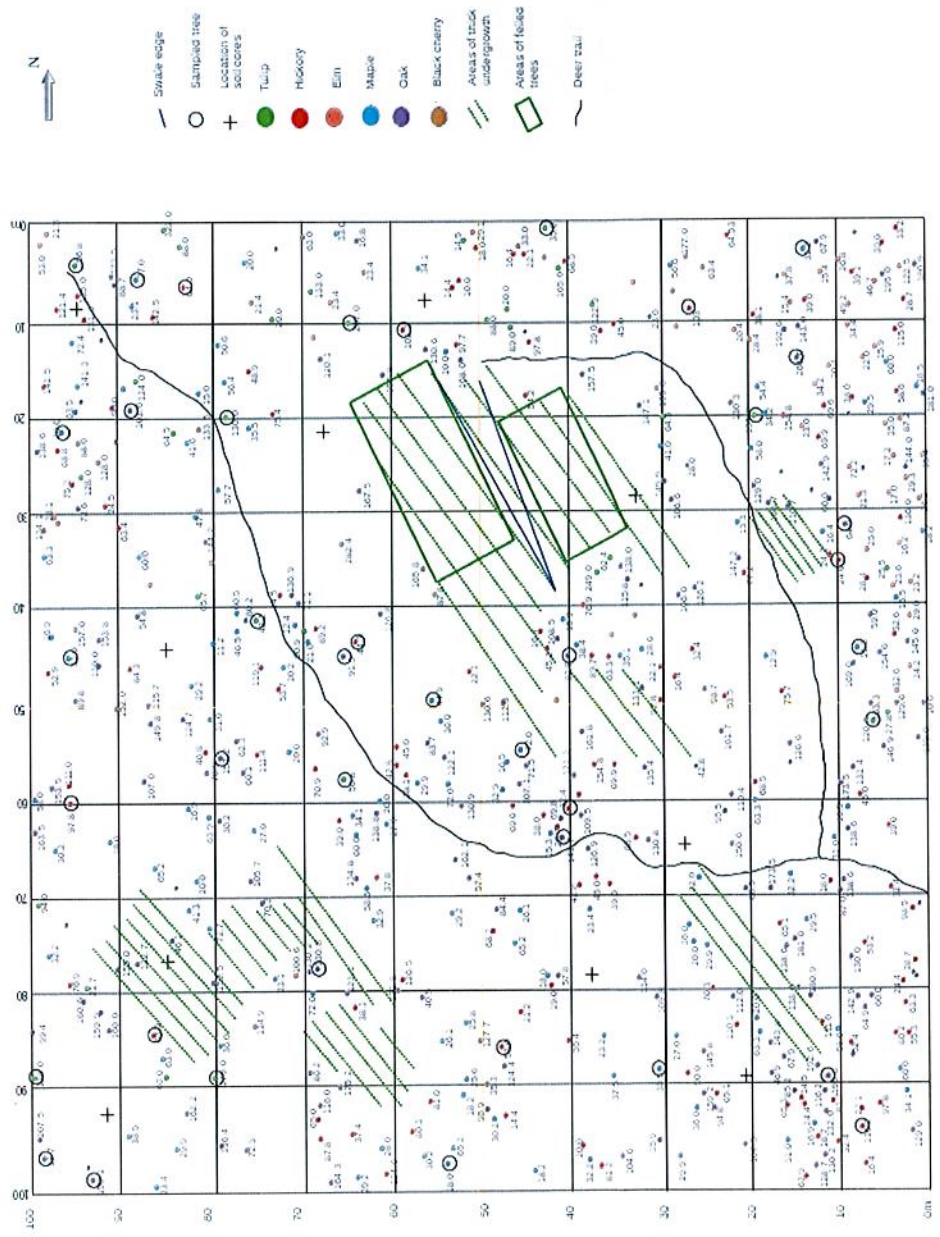


Illustration 11: Map of the 1 hectare field cite in Martell Forest, West Lafayette, Indiana. A larger map can be found in Appendix B.

### 2.2.2 Sampling Methods

This study aims to determine both the inventory and the flux of  $^{10}\text{Be}$  in a forest, and to compare this with the available  $^{10}\text{Be}$  stored in the soil. The inventory of  $^{10}\text{Be}_{\text{met}}$  in the trees can be determined by obtaining the concentration of  $^{10}\text{Be}_{\text{met}}$  in standing live trees and multiplying by the mass of trees on the plot. The  $^{10}\text{Be}$  flux through the biomass is set by the annual litterfall, including leaves, dead trees, and fallen limbs. I focus on the leaves, because leaf fall typically accounts for 75-80% of the total litterfall (Grizzard, Henderson, Clebsch, & Reichle, 1976). The annual flux is the product of the leaf fall mass and the  $^{10}\text{Be}$  concentration in the leaves. The soil inventory is estimated by analyzing  $^{10}\text{Be}$  and  $^{10}\text{Be}/^9\text{Be}$  in soil columns distributed across the plot.

#### 2.2.2.1 Trees

The dominant tree species in the hectare plot were *Carya ovalis* (red hickory), *Liriodendron tulipifera* (yellow poplar), *Quercus velutina* (black oak), and *Acer rubrum* (red maple). These tree species represent a full succession, with hickory and oak representing the late successions and the tulip and maple representing the early successions.

To determine the average Be contents in the four major species, I analyzed the stemwood from 10 trees of each species, combined into a single amalgamated and homogenized sample. The trees sampled were chosen based on a few features. The trees were selected to be various sizes, including both large and small individuals. They were also chosen based on location within the site to get a fair representation of the entire site, so trees were chosen from all over the site equally. The map insert (illus. 11) shows the location of major features of the hectare plot tested at Martell as well as the location and DBH of individual trees of the species analyzed. The map also shows the location of trees that samples were taken out of by a circle around the individual tree.

A cordless hand drill with an extended  $\frac{1}{4}$  inch (~6 mm) diameter drill bit was used to take a tree core from 10 individual trees of each of the four dominant species. I drilled

through the bark all the way down to the heartwood and collected the bark, cambium and wood in plastic bags as the shavings fell out of the tree. All 10 individual samples from each species were collected in the same bag and mixed thoroughly. The entire amalgamated sample was analyzed, so there was no need to homogenize it.

#### 2.2.2.2 Soils

Ten soil samples were taken randomly from throughout the site, at locations chosen by dropping markers (Skittles candy) on the map. The sites represent both soil types within the hectare, and are situated on high and low topography. Locations of soil samples are denoted by black X's on the map insert (illus. 11).

The soil cores were taken to a depth of 1 m. This was done with a 1 in (2.54 cm) round, 30 cm long soil corer down to a depth of 60 cm. Below this, the ground became too hard for the soil corer, and a bucket auger was used in 10 cm intervals over the last 40 cm. Each core was divided into 10 cm sections, and each section was put into its own plastic bag for transport. Then, the contents of each bag were placed in an aluminum baking tin, and dried at 70°C overnight. An aliquot of 2 g from each core was combined for every 10 cm depth interval. The amalgamated samples were homogenized and subsampled for analysis.

#### 2.2.2.3 Leaves and nuts

Leaf samples were collected in the autumn during the annual leaf fall, so that leaves were not decayed at the time of collection, and so that the 2011 leaf fall was clearly distinguishable from the previous years' leaf falls. One thousand leaves each of hickory, maple, oak and tulip were collected from the ground throughout the entire hectare over the span of a month. Each leaflet on the hickory compound leaf was counted

as one leaf. While there are different varieties of oak and maple, only black oak and sugar maple were collected and analyzed since they represented the majority of their species in the hectare plot. Tulip leaf collection was uncomplicated and the leaves were taken as is. In all cases, the stems were retained and analyzed with the leaf body.

Acorns and hickory nuts were collected just before and at the same time as leaf fall. Approximately 30 nuts of each type were collected to ensure a minimum of 20 g oven dried mass of each for analysis. Nuts were collected across the site, and from various topographic settings. Mixing and homogenizing was unnecessary due to all sample being used instead of an aliquot.

### 2.3 Sample digestion and beryllium chemistry

Processing the wood, nuts and leaves for the inventory portion of this project is a modified from a protocol used by the National Soil Erosion Lab to dissolve organic soils (Stott, 2010). The procedure for processing the soils, on the other hand, is a standard method of leaching out acid extractable elements combined with a modification from Rauret et al. (1999).

#### 2.3.1 Nuts

Nuts were dried at 70°C overnight and massed. For chemical digestion, the nuts were first ashed in an open nickel crucible over a Bunsen burner. I estimated the temperature of the crucible to be about 900°C (bright orange) for a majority of the burning process, which lasted 30-45 minutes. For the final 2 minutes of ashing, the gas was turned up so that the crucible turned white hot to burn away any left over organics, leaving only white ash behind. The ash was massed, then dissolved the same way as the wood and leaves, as explained below in section 2.3.3.

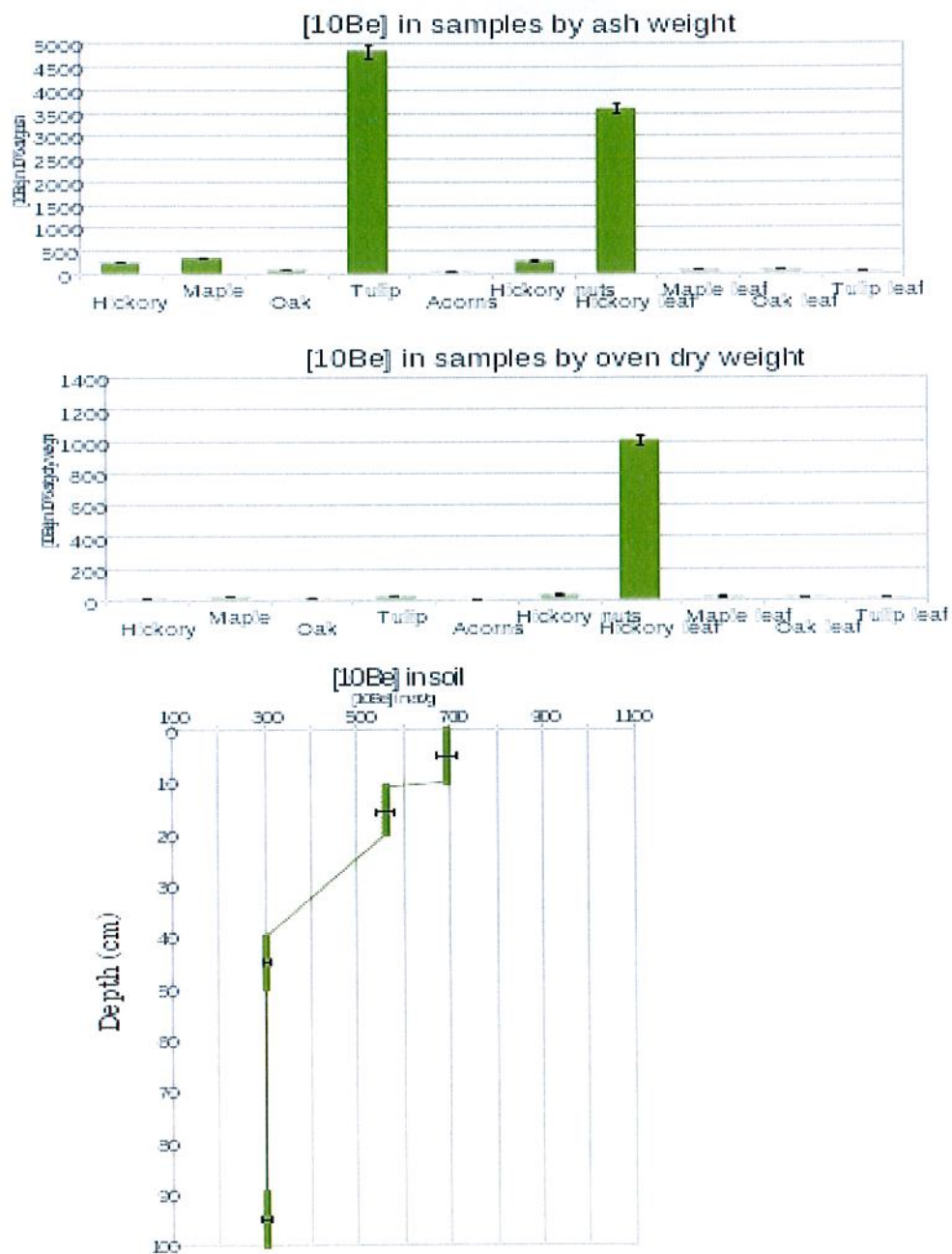
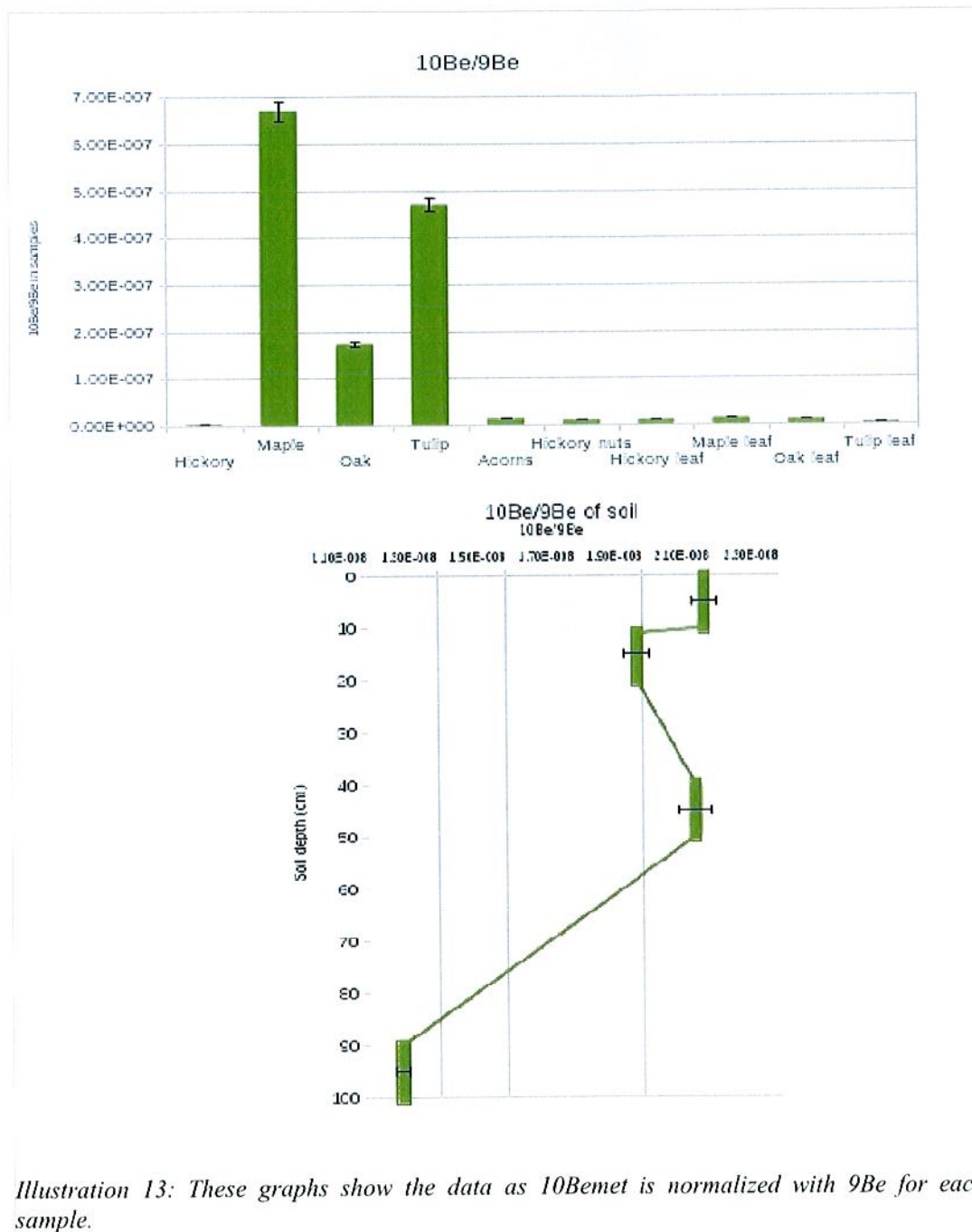


Illustration 12: These graphs show the  $[^{10}\text{Be}_{\text{met}}]$  in the samples. Hickory shows a possible bioaccumulation of  $^{10}\text{Be}_{\text{met}}$ , while the spike in tulip may be due to the unrepeatable, confounding error.



*Illustration 13: These graphs show the data as  $^{10}\text{Be}$  is normalized with  $^9\text{Be}$  for each sample.*

Wood shavings from the tree cores and the 1000 leaves from each species leaves were oven dried at  $70^\circ\text{C}$  overnight then massed. Leaves were ground to powder in a



coffee mill. The powder was then thoroughly mixed and split into 8 parts; the homogenized sample was taken evenly from each of the 8 parts to ensure that it was representative of the average. The leaf aliquot and the wood samples were ashed in ceramic crucibles with ceramic lids in a furnace at 900°C overnight. The samples were allowed to cool, mixed within the crucible, then ashed again at 900°C overnight. In most cases, the ash was white. The exception to this was the tulip sample, which had some black residue that would not burn away with repeated oven ashing. It is estimated that this sample had about 10% or less of what may be organic residue unashed at the time of dissolution.

### 2.3.3 Dissolution

Dissolution of the nuts, wood, and leaves were done in the same manner. A detailed, step by step protocol can be found in Appendix C. Ashed samples were first treated with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> to oxidize any remaining organics, heating and evaporating the sample to dryness and repeating until no black organic material remained. The remaining material was alternately fumed in H<sub>2</sub>SO<sub>4</sub> and HCl until total digestion had occurred. Samples of wood and nuts contained silica that did not dissolve in these acids; these were treated with HCl and then fumed in H<sub>2</sub>SO<sub>4</sub> to drive away any fluorides.

Following digestion and drydown, the samples were dissolved in 1:1 HCl and an aliquot taken for elemental analysis by ICP-OES. The remaining sample was spiked with <sup>9</sup>Be, and beryllium was isolated for AMS using standard methodologies as explained below.

### 2.3.4 Soils

The amalgamated soil samples were prepared for <sup>10</sup>Be<sub>met</sub> and <sup>10</sup>Be<sub>met</sub>/<sup>9</sup>Be analysis. Because <sup>10</sup>Be<sub>met</sub> is introduced from wet and dry deposition, we are interested in only the <sup>10</sup>Be<sub>met</sub> in secondary minerals or bound to soil and clay. Likewise, for <sup>10</sup>Be<sub>met</sub>/<sup>9</sup>Be analysis

we are interested in the beryllium that is available for uptake by plants, so we analyze only the exchangeable component or that in authigenic minerals.

Each sample was massed, and then exchangeable beryllium was extracted in a 0.5 M HCl solution for 6 hours at 60°C. Each soil sample was contained in a 50 ml centrifuge tube and was vortexed occasionally to ensure adequate mixing. Following extraction the supernatant solution was decanted into a second centrifuge tube.

Authigenic beryllium was extracted following our lab's procedures for analyzing authigenic iron minerals in soil. A solution of 0.5 mol l<sup>-1</sup> hydroxylamine hydrochloride (ACS) solution was freshly prepared. The soil was leached for 16 hours under continuous agitation on a shaker table. The leachate was combined with that from the acid leach, and an aliquot taken for beryllium determination by ICP-OES. The remaining solution was spiked with <sup>9</sup>Be, evaporated to dryness and converted to chloride form by repeated drydown in HCl. Beryllium was isolated for AMS using standard methodologies, uniform to all sample types.

### 2.3.5 Beryllium Chemistry

Following standard PRIME Lab procedures, each sample is converted to chloride form and taken up in 1:1 HCl. The solution is vigorously added to 12.5% NaOH solution to bring pH to >14, and vortexed for 1 minute. At this pH, beryllium and aluminum are in solution while many other elements including titanium and iron are precipitated. The sample is centrifuged, and the supernatant containing the beryllium is decanted to a second centrifuge tube and adjusted to pH 8 with HCl (buffered with 1 ml NH<sub>4</sub>OH). Beryllium (and aluminum) are precipitated as hydroxides, while Ca, Na, and Mg remain in solution. The supernatant solution is decanted, and the hydroxide gel rinsed twice in pure water.

The beryllium-containing gel is dissolved in 0.4 M oxalic acid and put onto a 2 ml cation exchange column (Dowex AG50W-X8). In this solution beryllium is held on the cation exchange column while aluminum (and nearly everything else) passes through.

The column is rinsed of oxalic acid with pure water. Any remaining Na is removed in 5 column volumes of 0.5 M HCl. Beryllium is then eluted in 5 column volumes of 1.2 M HCl. The solution is then brought to pH 9 with  $\text{NH}_4\text{OH}$  in the presence of EDTA to precipitate clean beryllium hydroxide. The beryllium hydroxide ( $\text{BeOH}$ ) gel is separated by centrifugation, and rinsed twice with pure water. The clean  $\text{BeOH}$  gel is then dried in a quartz glass vial, and calcined to  $\text{BeO}$  at  $1100^\circ\text{C}$  for one hour. The oxide is mixed with niobium and packed in stainless steel holders for analysis by AMS at PRIME Lab.

#### 2.4 Results

There are three ways which we reduce the data: concentration for dry weight, concentration for ash weight, and the  $^{10}\text{Be}/^9\text{Be}$  ratio. The oven dried weight shows the sample with all the mineral and organics, but without the water. Ash weight takes the weight of organics out of the equation, so what is left is the mineral weight. By looking at these raw amounts side by side with a known quantity of  $^9\text{Be}$ , we can compare them with the ratio of  $^{10}\text{Be}/^9\text{Be}$ .

The dry weights of the samples were taken after oven drying for 24 hours at  $70^\circ\text{C}$ . The ashed weights of the samples were taken after the samples were ashed at  $900^\circ\text{C}$  for 16 hours. Previous studies report their findings in relation to dry weights (Lundberg et al., 1983) and ashed weights (Klein et al., 1982). For this reason, I present both variations of the data so it can be compared. However, as can be seen by the figure (illus. 12), there is a large variation in quantity. By normalizing the data to the stable isotope beryllium-9, we can look at the data with less marked variation (illus. 13).

Most samples do not appear to retain Be in wood, leaves, or nuts. Hickory and tulip appear to be exceptions. However, an unknown confounding factor rendered the tulip data untrustworthy and unrepeatable, and so that data was not incorporated into our conclusions. The reason for hickory's exceptional nature, however, informs the turnover rate of Be as discussed in section 2.4.1.

#### 2.4.1 Modeling transfer factors and turnover rates

The transfer factors and turnover rates can be used to answer the original question posed at the beginning of this study: To what extent is  $^{10}\text{Be}_{\text{met}}$  truly immobile in the soil?

To calculate turnover times, we must first establish the relative mobility of beryllium in the soil (i.e., whether model A or model B, discussed in section 2.1.1, is more appropriate), and also the fraction of beryllium in the trees that is taken up from the exchangeable pool versus from mineral weathering.

Sample	[Be] (ng/g)	$^{10}\text{Be}/^9\text{Be}$ ( $\times 10^{-9}$ )	[ $^{10}\text{Be}$ ] ( $10^6$ at/g ash)
Soil 0-10 cm	490 $\pm$ 25	21.0 $\pm$ 1.1	700 $\pm$ 12
Soil 10-20 cm	450 $\pm$ 22	19.0 $\pm$ 1.0	560 $\pm$ 12
Soil 40-50 cm	220 $\pm$ 11	21.0 $\pm$ 1.1	300.0 $\pm$ 6.9
Soil 90-100 cm	380 $\pm$ 19	12.0 $\pm$ 0.6	300.0 $\pm$ 5.2
Hickory leaves	5500 $\pm$ 270	10.0 $\pm$ 0.7	3600 $\pm$ 180
Oak leaves	100.0 $\pm$ 5.0	9.50 $\pm$ .05	65.0 $\pm$ 1.7
Maple leaves	70.0 $\pm$ 4.0	13.0 $\pm$ 0.7	59.0 $\pm$ 1.1
Hickory nuts	430 $\pm$ 21	9.5 $\pm$ 0.5	270.0 $\pm$ 6.0
Acorns	25.0 $\pm$ 1.2	13.0 $\pm$ 0.8	21.0 $\pm$ 0.7

*Table 3: Beryllium concentrations in samples, as calculated from the data.*

It is clear from Table 3 that the  $^{10}\text{Be}/^9\text{Be}$  ratio in the exchangeable pool of the soil is relatively constant over the rooting depth. The ratio decreases at 1 meter depth, but this is below the depth of most roots. The soil at Martell is developed on glacial till, so it also contains significant inherited  $^{10}\text{Be}_{\text{met}}$  from the time of deposition that persists below the rooting depth (Balco & Rovey, 2008).

This  $^{10}\text{Be}_{\text{met}}/^9\text{Be}$  ratio in the rooting zone indicates that beryllium at our site is likely to be highly mobile within the rooting zone. Three samples from the surface to a depth of 50 cm yield an isotopic ratio of  $R_{\text{soil}} = (20.0 \pm 1.1) \times 10^{-9}$ . On the other hand, the leaves and nuts all have broadly similar but substantially lower isotopic ratios with an average value of  $R_{\text{leaf}} = (10.8 \pm 1.8) \times 10^{-9}$ . This indicates that the trees are deriving their beryllium from both the exchangeable pool of the soil and from mineral weathering or

Species	Transfer factor	Turnover time (ky)
Hickory	10.9	1.3
Oak	0.2	86
Maple	0.14	101

*Table 4: Transfer factors and turnover times per specie.*

from greater depth in the soil. Dividing  $R_{\text{leaf}}$  by  $R_{\text{soil}}$  yields an estimated value of the fraction of beryllium from the exchangeable pool  $f_{\text{exch}} = 0.54 \pm 0.09$ .

We can now calculate the transfer factors  $T_{\text{leaf}}$  for the three species analyzed. Because the profile indicates relatively mobile beryllium within the rooting zone, the transfer factors are calculated relative to the beryllium concentration at the surface. Table 4 shows the transfer factors for hickory, oak, and maple, based on beryllium concentrations by ash weight.

Remarkably, hickory trees are seen to bioaccumulate beryllium, with over 10 times higher concentration in hickory ash than in the exchangeable fraction of bulk soil. In contrast, oak and maple have transfer factors much smaller than unity. This behavior of hickory trees leads to rapid beryllium turnover in the soil.

Calculated turnover times are given in Table 4 assuming a  $^{10}\text{Be}$  e-folding length ( $1/k$ ) of 50 cm, a soil density of  $1.5 \text{ g cm}^{-3}$ , an averaged leaf flux of  $0.035 \text{ g cm}^{-2} \text{ yr}^{-1}$  dry weight. Hickory and maple samples had measured ash fractions of 28% by mass, while oak was 23% by mass.

Calculated turnover times yield remarkably different results for the tree species. Oak and maple have turnover times of approximately 100 ky. These species probably do not significantly affect  $^{10}\text{Be}$  profiles or beryllium concentrations in the soil over Holocene timescales, but may be important for very old soils. On the other hand, hickory trees have a turnover time of 1.3 ky. A single hickory tree that lives for 250 years can potentially turn over nearly 20% of the beryllium in the soil (and a far greater fraction if the  $^{10}\text{Be}$  profile is more shallow). A hickory forest can turn over 95% of the beryllium in the soil

within 4,000 years. Clearly, hickory is extremely important for cycling beryllium and meteoric  $^{10}\text{Be}$ .

Oak-hickory forests are a dominant biome over much of the eastern United States. The fraction of hickory in the forest typically ranges from 10-25% (R. B. Jackson et al., 1996). At our study site, hickories account for 21% of the trees. If we consider that the location of individual trees is random over thousands of years and that the fraction of hickories is constant, then the average turnover time of beryllium in the forest is 6,500 years. Hickories would have cycled through roughly half of available  $^{10}\text{Be}$  over the Holocene.

Is this behavior limited to hickory trees? The biogeochemical cycling of  $^{10}\text{Be}$  through the environment has been explored at only the most rudimentary level. Early work showed that  $^{10}\text{Be}$  was present in a maple leaves in small amounts (Klein et al., 1982), and in a piece of oak wood at a concentration of  $2 \times 10^6 \text{at/g}$  (Klein et al., 1982). A measurement of decayed organic matter in the Maurice River-Union Lake system showed the phenomenally high concentration of  $10^{10} \text{at/g}$ , one of the highest concentrations ever measured in terrestrial material (Lundberg et al., 1983). Beyond this exploratory work from over 25 years ago, there have been no published measurements of  $^{10}\text{Be}$  from natural living organisms. Thus it is unknown to what degree  $^{10}\text{Be}$  may be involved within natural ecosystems, and whether biogeochemical cycling could influence the soil  $^{10}\text{Be}$  inventory.

We have seen from previous studies (e.g. Brooks Jr., 1989; "Environmental Health Criteria 106: Beryllium," 1990; Grigor'yev, 1986a) that there can be a lot of beryllium accumulation. It is known that beryllium can be incorporated into living organisms, including tobacco ("Environmental Health Criteria 106: Beryllium," 1990), food plants ("Environmental Health Criteria 106: Beryllium," 1990), trees (Curtin, King, & Mosier, 1974; Dittmann, Höffel, Müller, & Neunhoeffer, 1984), grasses (Brooks Jr., 1989), and fungi (Gadd, 1999). As a crude rule of thumb, the beryllium concentration in plants (by ash weight) ranges from 0.01 – 1 ppm. Animals have also shown similar concentrations of beryllium with oysters having the highest concentration

("Environmental Health Criteria 106: Beryllium," 1990) and caterpillars and ants having lowest concentrations (Grigor'yev, 1986a).

Given that beryllium is known to be mobile within the environment and within soils (Brooks Jr., 1989; "Environmental Health Criteria 106: Beryllium," 1990; Grigor'yev, 1986a, 1986b), it could be expected that meteoric  $^{10}\text{Be}$  may be similarly mobile. In this paper, we report some initial measurements of  $^{10}\text{Be}$  in trees and soils at an experimental forest plot, and develop a simple model for beryllium cycling in deciduous trees to estimate the turnover time of  $^{10}\text{Be}$  within the forest soil.

## 2.5 Conclusions

This simple study looks at the natural cycle of  $^{10}\text{Be}_{\text{met}}$  over the course of one year. This snapshot would allow us to see if a tree were to draw up the meteoric beryllium and hold the element in the wood or if it would cycle it out of the system with the annual leaf fall. Since all the samples were taken during fall, it is reasonable to assume that any meteoric beryllium in the wood of the trees would not be pushed out into the leaves, which had already begun to fall. If there is little cosmogenic beryllium in the wood, but a lot in the freshly fallen leaves, then it is equally reasonable to assume that the tree pushes the beryllium out of the tree, where it will decay and recycle back into the system (illus. 1).

Our experiments showed that  $[^{10}\text{Be}_{\text{met}}]$  is highest in hickory leaves, regardless of being measured by ash weight or dry weight. The tulip may show a higher  $[^{10}\text{Be}_{\text{met}}]$  per ash weight because, when ashed, the tulip was light and fluffy. When reduced to a liquid, the amount was too small to analyze, and nearly 2.5 times the amount of wood was needed for the same amount of reduced sample that aliquots could be taken out of than any other sample. The rest of the wood, leaf, and nut samples showed a small amount of cosmogenic beryllium, but nothing extraordinary, which is comparable to the previous studies (Klein et al., 1982).

Cosmogenic beryllium concentrations in the soil profile suggests a that  $^{10}\text{Be}_{\text{met}}$  is added continuously at the top of the column, then eluted downward with the clay and particles and water solution. This indicates that there has been little erosion, and we can focus on the pathways of  $^{10}\text{Be}_{\text{met}}$  in the trees.

However, the concentration data shows that hickory can bioaccumulate  $^{10}\text{Be}_{\text{met}}$ , leaving questions of the overall mobility of  $^{10}\text{Be}_{\text{met}}$  through the geochemical cycle. There are also questions about being able to really use  $^{10}\text{Be}_{\text{met}}$  to study soil erosion provenance.



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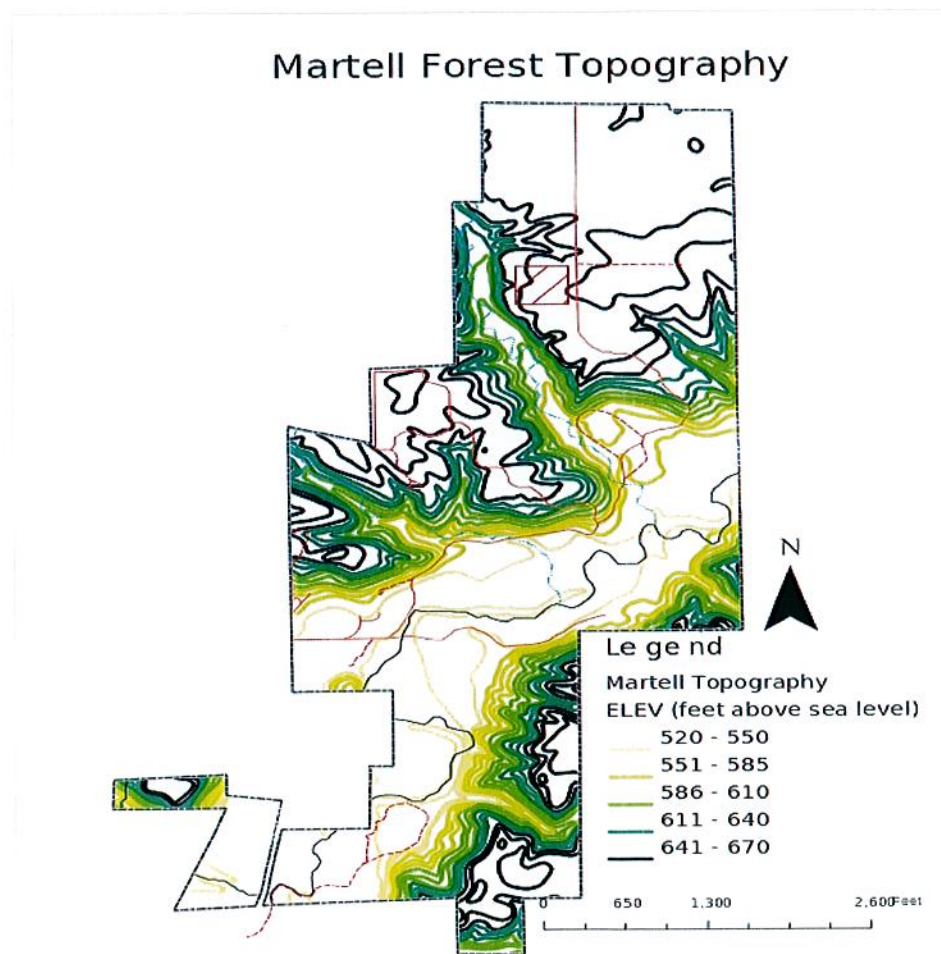
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## APPENDICES

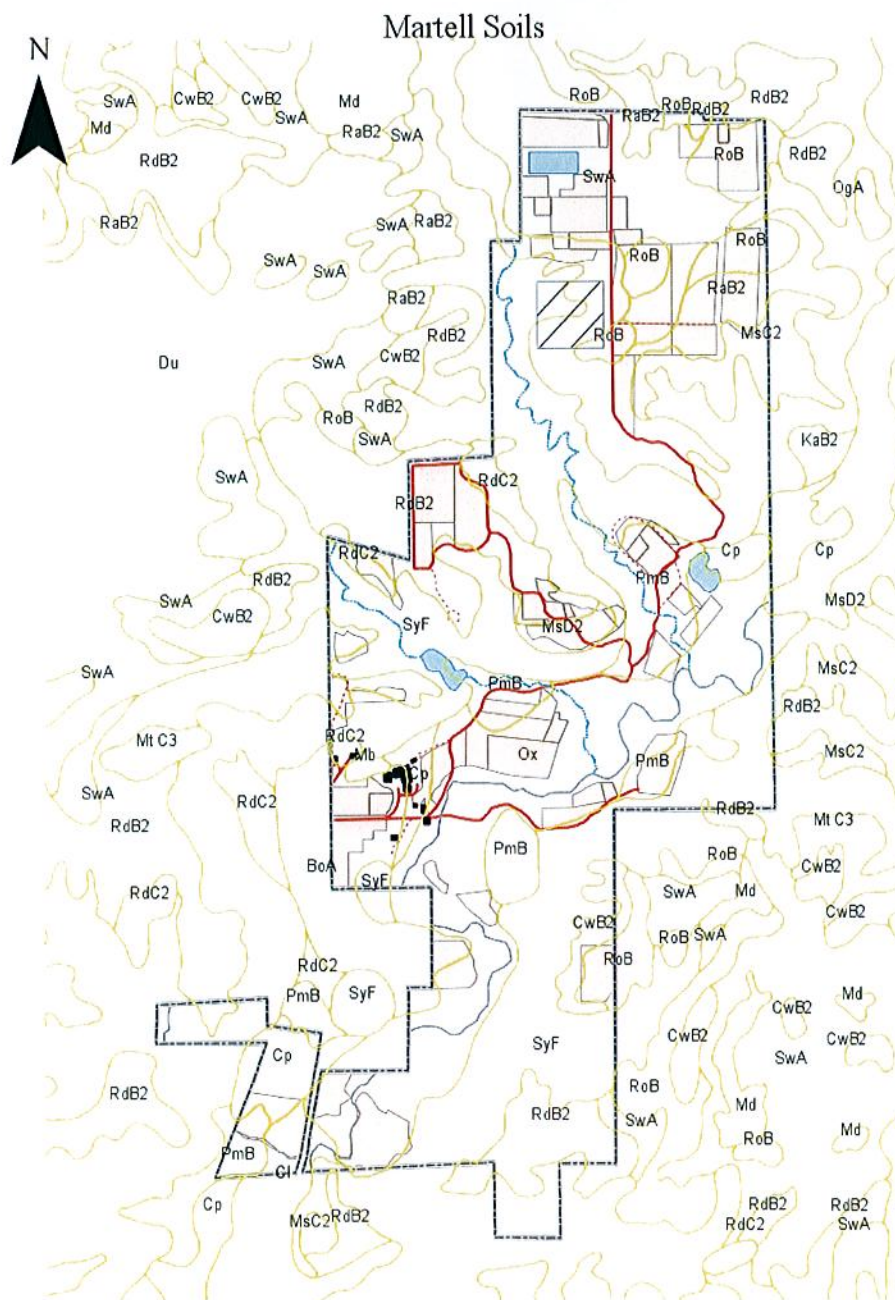
## Appendix A: Martell Forest Information and Maps

All maps in this section were obtained via personal communication with Burk Thompson, Martell Forest site manager, or Andrew Meier, former student working in the Martell office cataloging and organizing information about Martell Forest.

There are three maps: topography, soils, and an aerial from 2009. Each map has been modified to show the approximate location of my field site within Martell Forest.

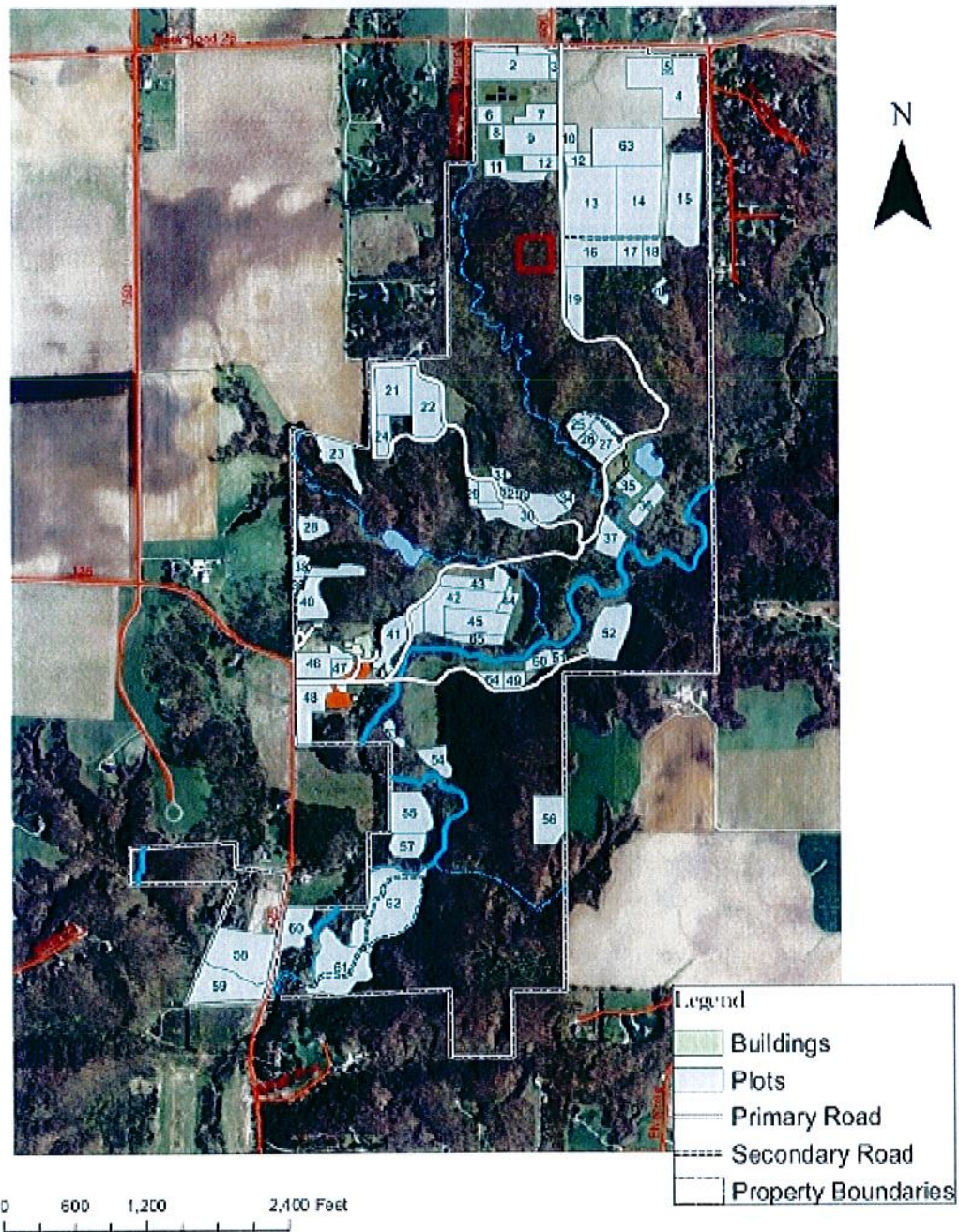


*Illustration A14: Topographic map of Martell Forest. My field site is denoted with a red, hashed box.*



*Illustration A15: Martel Forest soils map. My study site is marked with the black, hashed square.*

## Martell Forest Research Plantings, 2009



*Illustration A16: An aerial photograph of Martell Forest that shows their research plots in light blue. My field plot is denoted by the red square near research plot #16. Note the features of the surrounding area and that the erosional features are at a distance.*

Appendix B: Detailed map of field site

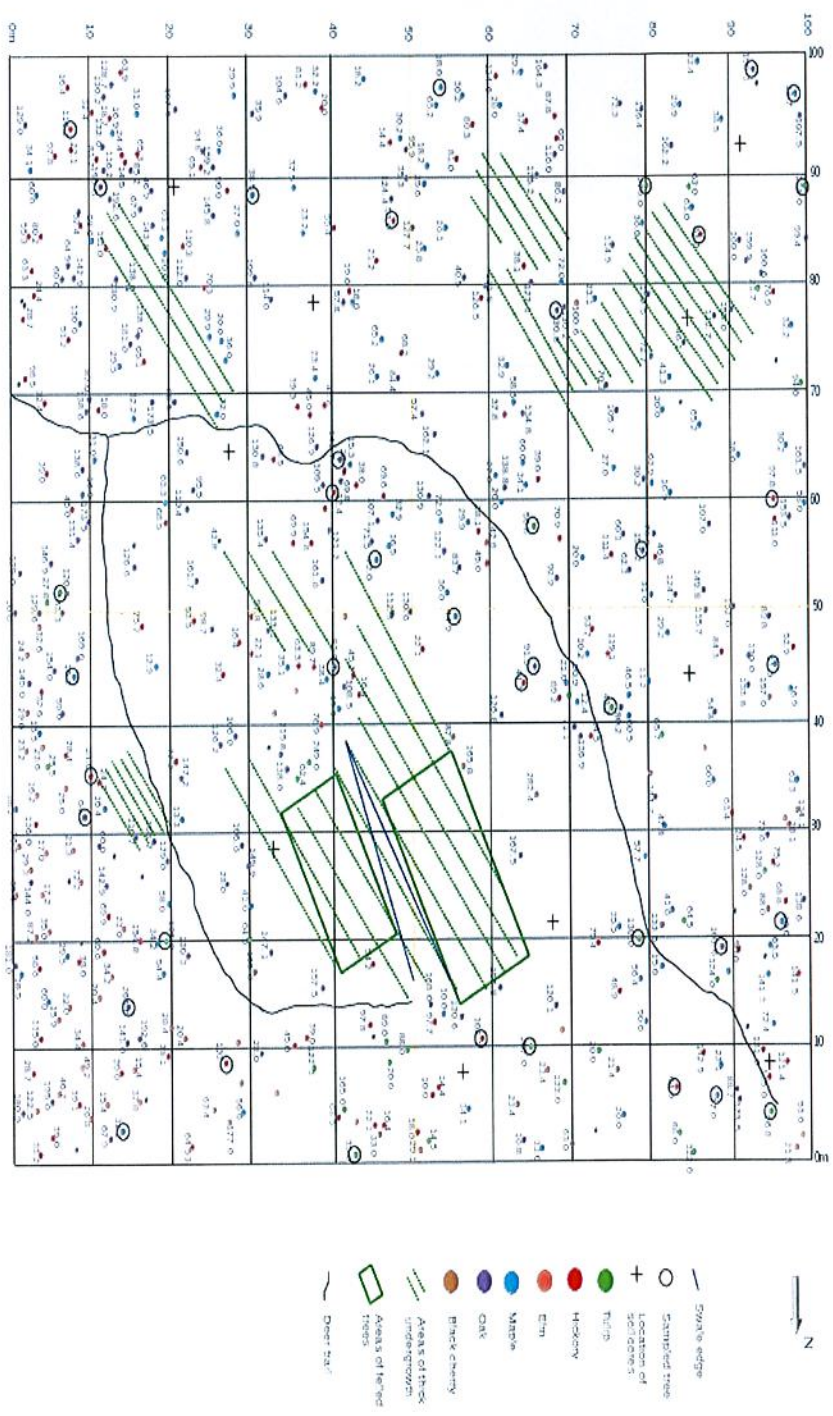


Illustration A17: Detailed map of my research site, mapped out as per description in chapter 2.



## Appendix C: Protocols

## Soil Extraction Protocol

From Rauet et al (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference material. J. Environ. Monit. 1, 57 – 61.

Extraction 1: Acetic acid

- \_\_\_\_\_ Add 0.5 g of sediment to a 50 mL centrifuge tube
- \_\_\_\_\_ Add 20 mL of 0.11 mol/ L acid acid solution
- \_\_\_\_\_ Shake for 16h at room temperature ( $22\pm 5^{\circ}\text{C}$ ) in end over end shaker
- \_\_\_\_\_ Centrifuge at 3000 g for 20 min.
- \_\_\_\_\_ Decant supernatant into a polypropylene container labeled XXXX; analyze immediately or store at  $4^{\circ}\text{C}$  until ready
- \_\_\_\_\_ Rinse sediment with 10 mL Pure water
- \_\_\_\_\_ Shake end over end for 15 min.
- \_\_\_\_\_ Centrifuge at 3000 g for 20 min.
- \_\_\_\_\_ Decant supernatant into a polypropylene container labeled XXXX; set aside in case needed, but will be discarded at end.

Extraction 2: Hydroxylammonium chloride

- \_\_\_\_\_ Add 20 mL of hydroxylammonium chloride
- \_\_\_\_\_ Vortex for 1 min
- \_\_\_\_\_ Shake for 16 h at room temperature ( $22\pm 5^{\circ}\text{C}$ ) in end over end shaker
- \_\_\_\_\_ Centrifuge at 3000 g for 20 min.
- \_\_\_\_\_ Decant supernatant into a polypropylene container labeled XXXX; analyze immediately or store at  $4^{\circ}\text{C}$  until ready
- \_\_\_\_\_ Rinse sediment with 10 mL Pure water
- \_\_\_\_\_ Shake end over end for 15 min.

\_\_\_\_\_ Centrifuge at 3000 g for 20 min.

\_\_\_\_\_ Decant supernatant into a polypropylene container labeled XXXX; set aside in case needed, but will be discarded at end.

Extraction 3: Hydrogen peroxide digestion and ammonium acetate extraction

\_\_\_\_\_ Add 5 mL of hydrogen peroxide slowly, cover loosely

\_\_\_\_\_ Digest at room temperature for 1 h, gently shaking occasionally

\_\_\_\_\_ Digest in water bath set to  $85\pm 2^{\circ}\text{C}$  for 1 h

\_\_\_\_\_ Uncover and reduce to less than 3 mL

\_\_\_\_\_ Add 5mL of hydrogen peroxide, cover loosely

\_\_\_\_\_ Digest in water bath set to  $85\pm 2^{\circ}\text{C}$  for 1 h

\_\_\_\_\_ Remove cover and reduce to ~1 mL. DO NOT TAKE TO DRYNESS

\_\_\_\_\_ Cool

\_\_\_\_\_ Add 25 mL of ammonium acetate

\_\_\_\_\_ Shake for 16 h at room temperature ( $22\pm 5^{\circ}\text{C}$ ) in end over end shaker

\_\_\_\_\_ Centrifuge at 3000 g for 20 min.

\_\_\_\_\_ Decant supernatant into a polypropylene container labeled XXXX; analyze immediately or store at  $4^{\circ}\text{C}$  until ready

Finished with sediment and may discard.

Protocol for dissolution and beryllium separation for fungi, fungal mats, and wood

Last edited by Grace Conyers on 28.May.2010

Sample # \_\_\_\_\_ Sample ID: \_\_\_\_\_ Shorthand:

\_\_\_\_\_

Preparation:

\_\_\_\_\_ Dunk sample wood or fungus into water for a few moments, then put into freezer to freeze overnight.

\_\_\_\_\_ Obtain volume of frozen wood or fungus with a graduated cylinder.

Volume: \_\_\_\_\_

\_\_\_\_\_ Dry sample in the oven at 50°C, mass: \_\_\_\_\_

\_\_\_\_\_ Ash sample in muffle furnace at 900°C or crucible over Bunsen burner, mass:

\_\_\_\_\_

Dissolving:

\_\_\_\_\_ Put sample in the Teflon liner for the acid bomb

\_\_\_\_\_ Add a few drops of sulphuric acid to wet the sample.

\_\_\_\_\_ Add 2 mL of nitric acid

\*Note:  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  will react a little. If the sample continues to fume, put it on a hot plate at setting 3 for 30 minutes – it is likely that the acids are reacting with the sample, not each other.

\_\_\_\_\_ Put lid on Teflon lining, place lining into acid bomb shell, and put the assembly into the oven at 150 – 200°C for 3 – 5 hours.

\_\_\_\_\_ Mass empty Teflon beaker with lid Mass: \_\_\_\_\_

\_\_\_\_\_ Transfer liquid sample to another Teflon vial with a screw-on lid.

\_\_\_\_\_ Rinse the Teflon liner from the acid bomb with 1 mL  $\text{NHO}_3$ , transfer to the Teflon vial with the sample

\_\_\_\_\_ Rinse liner out with 2 consecutive mLs of DIW and transfer to the Teflon vial.

\_\_\_\_\_ Mass Teflon beaker again with liquid. Mass: \_\_\_\_\_

Note: Sample should be completely dissolved, if it is not, follow the steps below.

\_\_\_\_\_ Evaporate as much as possible in the Teflon vial, then transfer to a fuming crucible to evaporate the sulphuric acid.

\_\_\_\_\_ Rinse the vial with .5 mL of sulphuric, then pour at the same place into the fuming crucible. Repeat once more.

\_\_\_\_\_ Evaporate down to dryness.

\_\_\_\_\_ Add 1 or 2 drops of perchloric acid and evaporate to dryness on a hot plate at 200 – 220°C.

\_\_\_\_\_ Allow to cool, then add 2 mLs HCl. Evaporate to dryness.

Note: Sometimes there are little “grains” on the bottom of the crucible or Teflon vial that will not dissolve. If these are present, fume in the fuming crucible with a couple mLs of HF.

\_\_\_\_\_ Once everything is dissolved, add 2 mLs HCl to the fuming crucible.

\_\_\_\_\_ Using a transfer pipette, draw up the HCl in the crucible and rinse down the sides with it.

\_\_\_\_\_ Using the transfer pipette, draw up the solution and put into a Teflon vial. Allow both the Teflon vial and fuming crucible to evaporate.

\_\_\_\_\_ Repeat the previous step until all of the sample has been put into the Teflon vial.

\_\_\_\_\_ Evaporate the sample in the Teflon vial to dryness.

\_\_\_\_\_ Label a 15 mL centrifuge tube “sample name” and mass the tube. (This will be the tube used for the carrier.) Mass: \_\_\_\_\_

\_\_\_\_\_ Add one mL of 1:1 HCl into the dried sample to dissolve and loosen.

\_\_\_\_\_ Put the dissolved mass + 1:1 HCl centrifuge tube, rinse Teflon vial out with DIW and pour into centrifuge tube.

\_\_\_\_\_ Dilute to 10 mL with DIW.

\_\_\_\_\_ Vortex thoroughly.

\_\_\_\_\_ Mass again. Mass: \_\_\_\_\_

Note: Occasionally the crystals will not redissolve in dilute acid, so put water into a glass beaker, put the sample in the centrifuge tube in the beaker, and put this on a hot plate on a low temperature. Be careful not to let the water get too hot or evaporate off completely.

Note: It may be necessary to add more 1:1 HCl or water. If this is necessary, always keep the same dilution factor.

#### Aliquot:

\_\_\_\_\_ Fill the "X OES" tube to 12 mL with DIW

\_\_\_\_\_ Mass again: \_\_\_\_\_

\_\_\_\_\_ Label and mass a 50 mL centrifuge tube "X ICP MS". Mass: \_\_\_\_\_

\_\_\_\_\_ Remove 1 mL from "X OES" and put into "X ICP MS" tubes, mass both

afterwards. Mass OES: \_\_\_\_\_ Mass ICP MS: \_\_\_\_\_

\_\_\_\_\_ Fill "X ICP MS" to 50 mL with 5% HNO<sub>3</sub>, then mass again.

Mass \_\_\_\_\_

#### Spike:

\_\_\_\_\_ Mass another 15 mL centrifuge tube for each sample and label "X OES". Mass:

\_\_\_\_\_

\_\_\_\_\_ Remove a 1 mL aliquot from the "sample name" centrifuge tubes and put into the massed "X OES" tube.

\_\_\_\_\_ Mass both the sample tubes and aliquot tubes. Mass sample: \_\_\_\_\_ Mass aliquot: \_\_\_\_\_

\_\_\_\_\_ Set aliquot tube off to the side.

\_\_\_\_\_ Spike "sample name" tubes with beryllium, so that the concentration of spike/#  $\mu\text{L} = .25 \mu\text{L}$ . (This is generally about .25 mL.) Mass again: \_\_\_\_\_

\_\_\_\_\_ Add ammonium hydroxide to "sample name tubes" until they are at pH 8. (Should smell like a dirty litter box.)

\_\_\_\_\_ Let the sample sit for 24 hours.

- \_\_\_\_\_ Centrifuge at 3800 RPM for 5 minutes.
- \_\_\_\_\_ Decant supernatant off into a 125 mL bottle labelled "X SUPN"
- \_\_\_\_\_ Rinse precipitate with 10 mL DIW and vortex.
- \_\_\_\_\_ Centrifuge at 3800 RPM for 5 minutes.
- \_\_\_\_\_ Decant supernatant off into a 125 mL bottle labelled "X SUPN"
- \_\_\_\_\_ Rinse precipitate with 10 mL DIW and vortex.
- \_\_\_\_\_ Centrifuge at 3800 RPM for 5 minutes.
- \_\_\_\_\_ Decant supernatant off into a 125 mL bottle labelled "X SUPN"
- \_\_\_\_\_ Dissolve gel in at least 2 mL of clean .4 M oxalic acid.\*\*

Note: If gel does not dissolve in the initial 2 mL of oxalic acid you can: 1.) add more oxalic acid, but not more than 6 mL; 2.) wait overnight to allow the oxalic acid to work. 3.) heat the centrifuge tube in a dry bath to allow the oxalic acid to work.

\*\*For fungi, the oxalic tends to make various oxalates. Let the sample sit over night to allow the oxalic acid to work. If there is still white gel or "sludge" at the bottom of the tube follow the directions below to see if the beryllium is in the solution.

- \_\_\_\_\_ Dilute the sample to 10 mL with DIW
- \_\_\_\_\_ Centrifuge at 3800 RPM for 5 minutes.
- \_\_\_\_\_ Decant supernatant off into a clean centrifuge tube and test the supernatant on the AA.

Be separation by cation exchange:

Note: column volume is 10 mL

When unpacking columns, check for bubbles in beads. If there are bubbles, tilt and tap the column to move beads into the reservoir and remove bubbles. Remove top first, then bottom tab.

### Condition column

- \_\_\_\_\_ Drain the resin bed.
- \_\_\_\_\_ Add 20 mL (2 column volumes) of 6N HCl and drain.
- \_\_\_\_\_ Add 6 mL (3 column volumes) of DIW and drain
- \_\_\_\_\_ (If columns are not to be used immediately, cap the bottom, add DIW up to the bend in the column, and put cap back on loosely.)

### Load the samples:

- \_\_\_\_\_ Place acid washed 60 mL bottle labelled "sample oxalic" below the columns
- \_\_\_\_\_ Load the columns with 1 mL of 0.4 M oxalic acid and drain.
- \_\_\_\_\_ Label the columns close to the top.
- \_\_\_\_\_ Using a transfer pipette, add sample solution from the "sample Be" tube to the top of the columns and drain.
- \_\_\_\_\_ Rinse centrifuge tube with 2 mL 0.4 M oxalic acid, vortex, then centrifuge for 5 minutes at  $> 3200\times g$  RCF.
- \_\_\_\_\_ Transfer rinsate to columns and drain.

Done with "sample Be" tubes – discard.

- \_\_\_\_\_ Add 10 mL 0.4 M oxalic acid to columns and drain.

### Cation columns (Beryllium)

- \_\_\_\_\_ Place "sample oxalic" bottle under column
- \_\_\_\_\_ Add 2 mL DIW and drain
- \_\_\_\_\_ Add 10 mL .5 N HCl and drain.
- \_\_\_\_\_ Replace "sample oxalic" bottle with 15mL centrifuge tube labelled "sample Be" under the column
- \_\_\_\_\_ Add 10 mL 1 N HCl and drain.
- \_\_\_\_\_ Replace 15 mL centrifuge tubes with bottle labelled "sample " under column

\_\_\_\_\_ With all tubes now open you can add the 10 drops of 10% EDTA solution to centrifuge tubes; invert to mix.

\_\_\_\_\_ Add 10 mL and drain

\_\_\_\_\_ Recondition the columns if it is to be used again.

#### Beryllium conversion to oxide

\_\_\_\_\_ If this step wasn't done earlier: add the 10 drops of 10% EDTA solution to centrifuge tubes, invert to mix.

\_\_\_\_\_ Adjust the pH to 8 or higher with ~25-30 drops of  $\text{NH}_4\text{OH}$

\_\_\_\_\_ Wait overnight (or an hour if really impatient)

\_\_\_\_\_ Centrifuge 15 mL "sample Be" tube for 5 minutes at  $> 3200xg$  RCF.

\_\_\_\_\_ Decant into the existing "sample supn" bottle.

\_\_\_\_\_ Add 7 mL DIW to the gel and vortex

\_\_\_\_\_ Centrifuge for 5 minutes

\_\_\_\_\_ Decant into the existing "sample supn" bottle

\_\_\_\_\_ Add 6 mL DIW and vortex.

\_\_\_\_\_ Centrifuge for 5 minutes

\_\_\_\_\_ Decant into the existing "sample supn" bottle.

\_\_\_\_\_ Make a map of block or fire-brick where each sample will be placed.

Note: centrifuge caps are not beryllium waste, but the centrifuge tubes, transfer pipettes, and the used gloves are. These go into a Ziploc bag labelled "Beryllium Oxide" with a hazardous waste sticker on it and into the hazardous waste bin.

\_\_\_\_\_ Take caps off all centrifuge tubes and add 3 drops of DIW from the dropper bottle into the tubes. Be careful not to touch the tip of the dropper to the tubes.

\_\_\_\_\_ Put a transfer pipette into each tube

\_\_\_\_\_ Put clean quartz glass vial into the block/fire-brick



\_\_\_\_\_ Mix the water/gel slurry and carefully transfer to the quartz glass vial. Do not allow slurry to enter the bulb of the pipette – it may not come back out and sample will be lost. Keep the tip of the pipette inside of the quartz glass vial when transferring; sometimes a bubble forms leaving beryllium hydroxide on the rim of the vial.

\_\_\_\_\_ Add three more drops of DIW from the dropper bottle to the centrifuge tubes.

\_\_\_\_\_ Mix the water and any remaining gel with the pipette and carefully transfer to the quartz glass vial.

\_\_\_\_\_ Dry vial overnight under heat lamps, no caps.

\_\_\_\_\_ (If the vials are not already on fire-brick, transfer over in the exact configuration as block)

\_\_\_\_\_ Add caps to vials

\_\_\_\_\_ Place the fire-brick into the muffle furnace and set the temperature to at least 900°C. Fire for one hour after the furnace hits 900°C.

\_\_\_\_\_ Turn oven off and let cool. Furnace can be cracked open slightly and carefully when the temperature falls below ~ 600°C.

#### Appendix D: Allometric equations of individual trees within the research site

Allometry was first coined by Julian Huxley and Georges Tessier in 1936 (Huxley & Tessier, 1936) to describe relative growth relationships between different parts of an organism over the course of its life. These allometric relationships are curvilinear in nature. However, they are linearized by replotting them on a log-log scale.

Allometric equations for trees can approximate the mass of above ground biomass of wood, stems, and foliage as well as the below ground biomass in the root system. With this information, we were able to approximate the amount of beryllium and  $^{10}\text{Be}_{\text{met}}$  which we used to model the transfer factors and turnover rates (§2.4.1). This appendix discusses the allometric equations we used and provides our raw data.

Allometric equations are developed on study sites, so there is more accuracy when using equations on similar sites to those which the equations were developed on. There were no allometric equations for Martell Forest, or even that of Indiana. Over the years that tree allometry studies have been done, a more generalized formulae based on dimensional analysis approach has been found to be fairly accurate. (Jenkins, Chojnacky, Heath, & Birdsey, 2003). Jenkins et al (2004) took this concept to develop allometric equations for 10 species groups of North American trees which predicts the oven-dried biomass of trees based on the DBH of trees with an  $R^2$  value of 0.938 and greater.

The four tree species in this manuscript fall within two of these groups Jenkins et al (2004) defined: Mixed hardwoods ( $R^2 = 0.980$ ) and hard maple/oak/hickory/beechn ( $R^2 = 0.988$ ). The allometric equations were used to approximate the total above ground oven-dried mass of the tree. Jenkins et al (2004) also provided an allometric equation based on the tree's DBH that would allow us to estimate the foliage mass only. We also used this to estimate the foliage despite an  $R^2$  value of 0.256 for hardwoods. We then subtracted the mass of foliage from the total above ground to obtain an estimation for the root mass.

The rest of the data in the table are our calculations of the  $[^9\text{Be}]$  and  $[^{10}\text{Be}_{\text{met}}]$  in the different parts of the tree using our collected data.

dbh (cm)	leaf mass (kg)	Tree mass (kg)		[9Bc] leaf		[9Bc] wood		9Bc total		9Bc litterfall		fraction in:		10Bc wood		10Bc leaf		10Bc total		10Bc litterfall		canopy area (m <sup>2</sup> )	Fallout rate (10 <sup>6</sup> at yr <sup>-1</sup> )	Tree inventory yr
		aboveground	belowground	total	(mg/kg)	(mg/kg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at)	(10 <sup>6</sup> at/kg)	(10 <sup>6</sup> at)	(10 <sup>6</sup> at/kg)						
8.15	0.77	22.09	7.29	30.15	1527.89	13.5	407.06	1172.72	2.881	7.35	832	2.22E+05	6.39E+05	30	300000	0.74								
40.29	21.10	1,079.71	356.30	1,457.11	1527.89	13.5	19670.98	32234.20	1.639	7.35	832	1.07E+07	1.76E+07	30	300000	35.71								
13.18	1.88	71.20	23.49	96.57	1527.89	13.5	1303.69	2869.48	2.201	7.35	832	7.10E+05	1.56E+06	30	300000	2.57								
36.62	16.97	856.14	282.53	1,155.64	1527.89	13.5	15601.17	25935.58	1.662	7.35	832	8.50E+06	1.41E+07	30	300000	28.32								
9.14	0.94	29.18	9.63	39.75	1527.89	13.5	536.63	1432.83	2.670	7.35	832	2.92E+05	7.80E+05	30	300000	0.97								
10.57	1.23	41.60	13.73	56.55	1527.89	13.5	763.49	1871.96	2.452	7.35	832	4.16E+05	1.02E+06	30	300000	1.59								
22.58	5.78	263.77	87.04	356.59	1527.89	13.5	4813.96	8829.84	1.834	7.35	832	2.62E+06	4.81E+06	30	300000	8.74								
12.42	1.67	61.56	20.32	83.55	1527.89	13.5	1127.91	2550.29	2.261	7.35	832	6.14E+05	1.39E+06	30	300000	2.05								
14.33	2.22	87.22	28.78	118.22	1527.89	13.5	1595.99	3391.99	2.125	7.35	832	8.69E+05	1.85E+06	30	300000	2.90								
13.65	2.01	77.20	25.48	104.68	1527.89	13.5	1413.23	3066.37	2.170	7.35	832	7.70E+05	1.67E+06	30	300000	2.57								
12.04	1.57	57.05	18.83	77.45	1527.89	13.5	1045.60	2399.27	2.295	7.35	832	5.69E+05	1.31E+06	30	300000	1.90								
12.13	1.59	58.16	19.19	78.95	1527.89	13.5	1065.84	2436.49	2.286	7.35	832	5.80E+05	1.33E+06	30	300000	1.93								
49.30	33.58	1,765.00	582.45	2,381.03	1527.89	13.5	32143.93	51305.54	1.596	7.35	832	1.75E+07	2.79E+07	30	300000	58.35								
22.17	5.55	252.15	83.21	340.91	1527.89	13.5	4602.27	8482.07	1.843	7.35	832	2.51E+06	4.62E+06	30	300000	8.35								
12.10	1.59	57.79	19.07	78.45	1527.89	13.5	1059.07	2424.05	2.289	7.35	832	5.77E+05	1.32E+06	30	300000	1.92								
22.26	5.60	254.80	84.08	344.49	1527.89	13.5	4650.62	8561.58	1.841	7.35	832	2.53E+06	4.66E+06	30	300000	8.44								
9.14	0.94	29.18	9.63	39.75	1527.89	13.5	536.63	1432.83	2.670	7.35	832	2.92E+05	7.80E+05	30	300000	0.97								
10.32	1.17	39.20	12.94	53.31	1527.89	13.5	719.69	1788.45	2.485	7.35	832	3.92E+05	9.74E+05	30	300000	1.31								
21.82	5.36	242.56	80.04	327.96	1527.89	13.5	4427.52	8194.27	1.851	7.35	832	2.41E+06	4.46E+06	30	300000	8.04								
12.42	1.67	61.56	20.32	83.55	1527.89	13.5	1127.91	2550.29	2.261	7.35	832	6.14E+05	1.39E+06	30	300000	2.05								
14.33	2.22	87.22	28.78	118.22	1527.89	13.5	1595.99	3391.99	2.125	7.35	832	8.69E+05	1.85E+06	30	300000	2.90								
13.65	2.01	77.20	25.48	104.68	1527.89	13.5	1413.23	3066.37	2.170	7.35	832	7.70E+05	1.67E+06	30	300000	2.57								
16.88	3.11	129.90	42.87	175.87	1527.89	13.5	2374.26	4748.31	2.000	7.35	832	1.29E+06	2.59E+06	30	300000	4.31								
6.75	0.56	13.96	4.61	19.13	1527.89	13.5	258.27	860.68	3.333	7.35	832	1.41E+05	4.69E+05	30	300000	0.47								
4.59	0.33	5.45	1.80	7.57	1527.89	13.5	102.24	506.53	4.954	7.35	832	5.57E+04	2.76E+05	30	300000	0.19								
6.37	0.52	12.11	4.00	16.63	1527.89	13.5	224.47	786.94	3.506	7.35	832	1.08E+05	3.97E+05	30	300000	0.36								
4.62	0.33	5.54	1.83	7.70	1527.89	13.5	103.94	510.60	4.912	7.35	832	1.22E+05	4.29E+05	30	300000	0.41								
6.05	0.48	10.69	3.53	14.70	1527.89	13.5	198.42	729.15	3.675	7.35	832	1.08E+05	3.97E+05	30	300000	0.36								
7.77	0.71	19.66	6.49	26.85	1527.89	13.5	362.50	1081.05	2.982	7.35	832	1.97E+05	5.89E+05	30	300000	0.66								
17.64	3.41	144.68	47.75	195.84	1527.89	13.5	2643.83	5209.59	1.970	7.35	832	1.44E+06	2.84E+06	30	300000	4.80								
22.39	5.67	258.37	85.26	349.90	1527.89	13.5	4715.56	8668.30	1.838	7.35	832	2.57E+06	4.72E+06	30	300000	8.56								
25.86	7.78	366.96	121.10	495.84	1527.89	13.5	6693.86	11885.19	1.776	7.35	832	3.65E+06	6.47E+06	30	300000	12.15								
20.80	4.84	215.89	71.24	291.97	1527.89	13.5	3941.64	7390.44	1.875	7.35	832	2.15E+06	4.02E+06	30	300000	7.15								
26.02	7.88	372.49	122.92	503.30	1527.89	13.5	6794.49	12047.35	1.773	7.35	832	3.70E+06	6.56E+06	30	300000	12.33								

*Carya ovata*

dbh (cm)	leaf mass (kg)	Tree mass (kg)			gBe total (mg)	gBe litterfall (mg)	fraction in litterfall	10Be total (10 <sup>-6</sup> at)	10Be litterfall (10 <sup>-6</sup> at/kg)	canopy area (m <sup>2</sup> )	Fallout rate 10 <sup>-6</sup> at/yr	Tree inventory yr
		aboveground	belowground	total								
30.00	10.82	526.77	173.83	711.43	9604.27	16533.82	1.722	5.23E+06	9.00E+06	30	300000	17.43
4.59	0.33	5.45	1.80	7.57	102.24	506.53	4.954	5.57E+04	2.76E+05	30	300000	0.19
6.37	0.52	12.11	4.00	16.63	224.47	786.94	3.506	1.22E+05	4.29E+05	30	300000	0.41
4.62	0.33	5.54	1.83	7.70	103.94	510.60	4.912	5.66E+04	2.78E+05	30	300000	0.19
5.73	0.44	9.37	3.09	12.91	174.27	674.70	3.872	9.49E+04	3.67E+05	30	300000	0.32
7.77	0.71	19.66	6.49	26.85	362.50	1081.05	2.982	1.97E+05	5.89E+05	30	300000	0.66
52.80	39.37	2,086.03	688.39	2,813.79	37986.15	60159.09	1.584	2.07E+07	3.28E+07	30	300000	68.95
20.38	4.63	205.58	67.84	278.05	3753.70	7077.93	1.886	2.04E+06	3.85E+06	30	300000	6.81
45.38	27.73	1,442.84	476.14	1,946.71	26280.60	42374.96	1.612	1.43E+07	2.31E+07	30	300000	47.70
7.10	0.61	15.79	5.21	21.61	291.75	932.52	3.196	1.59E+05	5.08E+05	30	300000	0.53
16.88	3.11	129.90	42.87	175.87	2374.26	4748.31	2.000	1.29E+06	2.59E+06	30	300000	4.31
38.66	19.20	976.79	322.34	1,318.34	17797.52	29341.03	1.649	9.69E+06	1.60E+07	30	300000	32.30
41.72	22.86	1,175.60	387.95	1,586.41	21416.51	34921.52	1.631	1.17E+07	1.90E+07	30	300000	38.87
42.99	24.49	1,264.91	417.42	1,706.82	23042.01	37417.67	1.624	1.25E+07	2.04E+07	30	300000	41.82
41.72	22.86	1,175.60	387.95	1,586.41	21416.51	34921.52	1.631	1.17E+07	1.90E+07	30	300000	38.87
16.62	3.01	125.18	41.31	169.49	2288.18	4600.22	2.010	1.25E+06	2.51E+06	30	300000	4.15
45.06	27.29	1,418.32	468.04	1,913.65	25834.25	41692.98	1.614	1.41E+07	2.27E+07	30	300000	46.89
23.95	6.57	304.42	100.46	411.45	5554.52	10039.98	1.808	3.02E+06	5.47E+06	30	300000	10.08
25.54	7.57	356.06	117.50	481.13	6495.24	11564.78	1.781	3.54E+06	6.30E+06	30	300000	11.79
21.91	5.41	245.15	80.90	331.47	4474.78	8272.17	1.849	2.44E+06	4.50E+06	30	300000	8.12
7.80	0.71	19.85	6.55	27.12	366.10	1088.50	2.973	1.99E+05	5.93E+05	30	300000	0.66
26.18	7.99	378.06	124.76	510.82	6896.01	12210.81	1.771	3.76E+06	6.65E+06	30	300000	12.52
24.27	6.76	314.37	103.74	424.87	5735.75	10334.72	1.802	3.12E+06	5.63E+06	30	300000	10.41
22.93	5.98	273.84	90.37	370.18	4997.47	9130.63	1.827	2.72E+06	4.97E+06	30	300000	9.07
25.92	7.82	369.17	121.83	498.81	6734.00	11949.90	1.775	3.67E+06	6.51E+06	30	300000	12.22
31.27	11.88	582.89	192.35	787.12	10626.16	18149.70	1.708	5.79E+06	9.88E+06	30	300000	19.29
17.83	3.49	148.53	49.01	201.03	2713.91	5328.94	1.964	1.48E+06	2.90E+06	30	300000	4.93
20.06	4.48	197.85	65.29	267.61	3612.80	6842.99	1.894	1.97E+06	3.73E+06	30	300000	6.56
27.96	9.25	443.85	146.47	599.57	8094.25	14131.78	1.746	4.41E+06	7.70E+06	30	300000	14.69
20.70	4.79	213.49	70.45	288.73	3897.79	7317.60	1.877	2.12E+06	3.98E+06	30	300000	7.08
11.91	1.54	55.60	18.35	75.48	1018.98	2350.18	2.306	5.55E+05	1.28E+06	30	300000	1.85
25.80	7.74	364.77	120.37	492.88	6653.85	11820.69	1.777	3.62E+06	6.44E+06	30	300000	12.08
25.57	7.59	357.14	117.86	482.59	6514.94	11596.58	1.780	3.55E+06	6.31E+06	30	300000	11.83
39.68	20.38	1,040.66	343.42	1,404.45	18960.10	31137.55	1.642	1.03E+07	1.70E+07	30	300000	34.42

## Carya ovalis cont.

dbh (cm)	leaf mass (kg)	aboveground	belowground	total	[9Be] leaf (mg/kg)	[9Be] wood (mg/kg)	9Be total (mg)	9Be litterfall (mg)	litterfall fraction in (10 <sup>-6</sup> at/g)	10Be wood (10 <sup>-6</sup> at/g)	10Be leaf (10 <sup>-6</sup> at/g)	10Be total (10 <sup>-6</sup> at)	10Be litterfall (10 <sup>-6</sup> at/kg)	canopy area (m <sup>2</sup> )	Fallout rate 10 <sup>-6</sup> at/yr	Tree inventory yr
35.13	15.44	773.45	255.24	1,044.12	1527.89	13.5	14095.68	23591.36	1.674	7.35	832	7.68E+06	1.28E+07	30	300000	25.59
28.66	9.77	471.41	155.57	636.75	1527.89	13.5	8596.19	14932.32	1.737	7.35	832	4.68E+06	8.13E+06	30	300000	15.60
20.73	4.81	214.29	70.71	289.81	1527.89	13.5	3912.37	7341.83	1.877	7.35	832	2.13E+06	4.00E+06	30	300000	7.10
20.35	4.62	204.80	67.58	277.00	1527.89	13.5	3739.46	7054.22	1.886	7.35	832	2.04E+06	3.84E+06	30	300000	6.79
5.96	0.47	10.29	3.39	14.15	1527.89	13.5	190.98	712.47	3.731	7.35	832	1.04E+05	3.88E+05	30	300000	0.35
10.32	1.17	39.20	12.94	53.31	1527.89	13.5	719.69	1788.45	2.485	7.35	832	3.92E+05	9.74E+05	30	300000	1.31
5.22	0.39	7.47	2.47	10.33	1527.89	13.5	139.43	594.52	4.264	7.35	832	7.59E+04	3.24E+05	30	300000	0.25
7.04	0.60	15.45	5.10	21.15	1527.89	13.5	285.48	919.15	3.220	7.35	832	1.55E+05	5.01E+05	30	300000	0.52
31.15	11.77	577.13	190.45	779.35	1527.89	13.5	10521.22	17984.09	1.709	7.35	832	5.73E+06	9.79E+06	30	300000	19.10
35.35	15.66	785.45	259.20	1,060.31	1527.89	13.5	14314.21	23932.19	1.672	7.35	832	7.79E+06	1.30E+07	30	300000	25.98
16.69	3.03	126.35	41.69	171.08	1527.89	13.5	2309.52	4636.98	2.008	7.35	832	1.26E+06	2.53E+06	30	300000	4.19
<b>TOTAL</b>	<b>5.38E+02</b>	<b>26,086.88</b>	<b>8.61E+03</b>	<b>3.52E+04</b>								<b>2.59E+08</b>	<b>4.48E+08</b>			

<i>Liriodendron tulipifera</i>																
dbh	leaf mass	Tree mass (kg)			[9Be] leaf	[9Be] wood	9Be total	9Be litterfall	fraction in litterfall	10Be wood	10Be leaf	10Be total	10Be in litterfall	canopy area	Fallout rate	Tree inventory
(cm)	(kg)	aboveground	belowground	total	(mg/kg)	(mg/kg)	(mg)	(mg)	(10 <sup>-6</sup> at/g)	(10 <sup>-6</sup> at/g)	(10 <sup>-6</sup> at)	(10 <sup>-6</sup> at)	(m <sup>2</sup> )	10 <sup>6</sup> at/yr	yr	
40.76	16.30	835.76	275.80	1,127.86	23.82	0.77	868.45	388.33	0.447	0.45	14	5.10E+05	2.28E+05	30	300000	1.70
56.37	35.03	1,869.25	616.85	2,521.13	23.82	0.77	1941.27	834.52	0.430	0.45	14	1.14E+06	4.90E+05	30	300000	3.80
20.06	3.25	143.71	47.42	194.39	23.82	0.77	149.68	77.49	0.518	0.45	14	8.80E+04	4.55E+04	30	300000	0.29
88.85	104.41	5,787.39	1,909.84	7,801.64	23.82	0.77	6007.26	2487.06	0.414	0.45	14	3.53E+06	1.46E+06	30	300000	11.77
10.51	0.85	28.84	9.52	39.21	23.82	0.77	30.20	20.30	0.672	0.45	14	1.77E+04	1.19E+04	30	300000	0.06
91.40	111.80	6,208.33	2,048.75	8,368.87	23.82	0.77	6444.03	2663.03	0.413	0.45	14	3.79E+06	1.57E+06	30	300000	12.62
28.66	7.22	348.49	115.00	470.71	23.82	0.77	362.45	172.09	0.475	0.45	14	2.13E+05	1.01E+05	30	300000	0.71
52.80	30.00	1,589.14	524.42	2,143.56	23.82	0.77	1650.54	714.49	0.433	0.45	14	9.70E+05	4.20E+05	30	300000	3.23
42.36	17.83	919.20	303.34	1,240.37	23.82	0.77	955.09	424.79	0.445	0.45	14	5.61E+05	2.50E+05	30	300000	1.87
6.37	0.35	8.32	2.74	11.41	23.82	0.77	8.79	8.42	0.958	0.45	14	5.17E+03	4.95E+03	30	300000	0.02
28.03	6.86	329.57	108.76	445.19	23.82	0.77	342.80	163.51	0.477	0.45	14	2.01E+05	9.61E+04	30	300000	0.67
102.55	147.74	8,262.00	2,726.46	11,136.20	23.82	0.77	8574.87	3519.24	0.410	0.45	14	5.04E+06	2.07E+06	30	300000	16.80
18.09	2.60	111.11	36.67	150.37	23.82	0.77	115.79	61.86	0.534	0.45	14	6.81E+04	3.64E+04	30	300000	0.23
40.76	16.30	835.76	275.80	1,127.86	23.82	0.77	868.45	388.33	0.447	0.45	14	5.10E+05	2.28E+05	30	300000	1.70
20.54	3.43	152.36	50.28	206.06	23.82	0.77	158.67	81.60	0.514	0.45	14	9.33E+04	4.80E+04	30	300000	0.31
43.31	18.79	971.56	320.61	1,310.96	23.82	0.77	1009.44	447.61	0.443	0.45	14	5.93E+05	2.63E+05	30	300000	1.98
38.95	14.66	746.36	246.30	1,007.32	23.82	0.77	775.63	349.13	0.450	0.45	14	4.56E+05	2.05E+05	30	300000	1.52
52.55	29.65	1,570.17	518.16	2,117.98	23.82	0.77	1630.84	706.34	0.433	0.45	14	9.59E+05	4.15E+05	30	300000	3.20
19.87	3.19	140.33	46.31	189.83	23.82	0.77	146.17	75.89	0.519	0.45	14	8.59E+04	4.46E+04	30	300000	0.29
79.30	79.34	4,363.01	1,439.79	5,882.14	23.82	0.77	4529.25	1889.96	0.417	0.45	14	2.66E+06	1.11E+06	30	300000	8.87
11.15	0.96	33.38	11.02	45.35	23.82	0.77	34.92	22.76	0.652	0.45	14	2.05E+04	1.34E+04	30	300000	0.07
28.34	7.04	338.95	111.85	457.85	23.82	0.77	352.54	167.77	0.476	0.45	14	2.07E+05	9.86E+04	30	300000	0.69
6.37	0.35	8.32	2.74	11.41	23.82	0.77	8.79	8.42	0.958	0.45	14	5.17E+03	4.95E+03	30	300000	0.02
28.03	6.86	329.57	108.76	445.19	23.82	0.77	342.80	163.51	0.477	0.45	14	2.01E+05	9.61E+04	30	300000	0.67
18.09	2.60	111.11	36.67	150.37	23.82	0.77	115.79	61.86	0.534	0.45	14	6.81E+04	3.64E+04	30	300000	0.23
39.49	15.14	772.39	254.89	1,042.42	23.82	0.77	802.66	360.56	0.449	0.45	14	4.72E+05	2.12E+05	30	300000	1.57
20.54	3.43	152.36	50.28	206.06	23.82	0.77	158.67	81.60	0.514	0.45	14	9.33E+04	4.80E+04	30	300000	0.31
41.40	16.90	868.57	286.63	1,172.10	23.82	0.77	902.52	402.68	0.446	0.45	14	5.30E+05	2.37E+05	30	300000	1.77
<b>TOTAL</b>	<b>7.03E+02</b>	<b>37.835.29</b>	<b>1.25E+04</b>	<b>5.10E+04</b>								<b>2.31E+07</b>	<b>9.84E+06</b>			

<i>Quercus velutina</i>															
dbh	leaf mass	Tree mass (kg)		[9Be] leaf	[9Be] wood	9Be total	9Be litterfall	fraction in litterfall	10Be wood	10Be leaf	10Be total	10Be in litterfall	canopy area	Fallout rate	Tree inventory
(cm)	(kg)	aboveground	belowground	(mg/kg)	(mg/kg)	(mg)	(mg)	(10 <sup>-6</sup> at/g)	(10 <sup>-6</sup> at/g)	(10 <sup>-6</sup> at/g)	(10 <sup>-6</sup> at)	(m <sup>2</sup> )	10 <sup>6</sup> at/yr	yr	
53.82	41.16	2,185.39	721.18	2,947.74	24.21	1120.14	996.55	0.890	0.22	13.8	6.38E+05	5.68E+05	30	300000	2.13
36.50	16.84	848.91	280.14	1,145.89	24.21	455.44	407.72	0.936	0.22	13.8	2.48E+05	2.32E+05	30	300000	0.83
45.86	28.41	1,480.09	488.43	1,996.93	24.21	758.83	687.85	0.906	0.22	13.8	4.33E+05	3.92E+05	30	300000	1.44
57.64	48.29	2,582.57	852.25	3,483.10	24.21	1323.58	1169.16	0.883	0.22	13.8	7.54E+05	6.66E+05	30	300000	2.51
57.61	48.23	2,579.09	851.10	3,478.42	24.21	1321.80	1167.65	0.883	0.22	13.8	7.53E+05	6.66E+05	30	300000	2.51
62.10	57.47	3,096.10	1,021.71	4,175.29	24.21	1586.61	1391.41	0.877	0.22	13.8	9.04E+05	7.93E+05	30	300000	3.01
61.34	55.83	3,004.16	991.37	4,051.36	24.21	1539.52	1351.68	0.878	0.22	13.8	8.78E+05	7.70E+05	30	300000	2.93
21.62	5.26	237.42	78.35	321.03	24.21	121.99	127.39	1.044	0.22	13.8	4.25E+04	7.26E+04	30	300000	0.23
45.54	27.96	1,455.19	480.21	1,963.37	24.21	746.08	676.89	0.907	0.22	13.8	4.25E+05	3.86E+05	30	300000	1.42
84.71	119.33	6,592.81	2,175.63	8,887.76	24.21	3377.35	2888.90	0.855	0.22	13.8	1.93E+06	1.65E+06	30	300000	6.42
45.51	27.91	1,452.72	479.40	1,960.03	24.21	744.81	675.80	0.907	0.22	13.8	4.25E+05	3.85E+05	30	300000	1.42
19.11	4.04	175.69	57.98	237.70	24.21	90.33	97.71	1.082	0.22	13.8	5.15E+04	5.57E+04	30	300000	0.17
20.67	4.77	212.69	70.19	287.65	24.21	109.31	115.57	1.057	0.22	13.8	6.23E+04	6.59E+04	30	300000	0.21
41.08	22.06	1,132.39	373.69	1,528.14	24.21	580.69	534.17	0.920	0.22	13.8	3.31E+05	3.04E+05	30	300000	1.10
55.25	43.76	2,329.76	768.82	3,142.34	24.21	1194.09	1059.37	0.887	0.22	13.8	6.81E+05	6.04E+05	30	300000	2.27
44.14	26.02	1,348.59	445.04	1,819.65	24.21	691.47	629.88	0.911	0.22	13.8	3.94E+05	3.59E+05	30	300000	1.31
44.14	26.02	1,348.59	445.04	1,819.65	24.21	691.47	629.88	0.911	0.22	13.8	3.94E+05	3.59E+05	30	300000	1.31
27.71	9.06	434.07	143.24	586.38	24.21	222.82	219.41	0.985	0.22	13.8	1.27E+05	1.25E+05	30	300000	0.42
41.40	22.46	1,153.88	380.78	1,557.11	24.21	591.70	543.71	0.919	0.22	13.8	3.37E+05	3.10E+05	30	300000	1.12
48.98	33.08	1,737.38	573.33	2,343.79	24.21	890.64	800.85	0.899	0.22	13.8	5.08E+05	4.56E+05	30	300000	1.69
27.01	8.56	407.84	134.59	550.98	24.21	209.37	207.29	0.990	0.22	13.8	1.19E+05	1.18E+05	30	300000	0.40
42.04	23.26	1,197.57	395.20	1,616.02	24.21	614.09	563.08	0.917	0.22	13.8	3.50E+05	3.21E+05	30	300000	1.17
41.46	22.54	1,158.20	382.21	1,562.95	24.21	593.92	545.63	0.919	0.22	13.8	3.39E+05	3.11E+05	30	300000	1.13
40.99	21.95	1,125.99	371.58	1,519.51	24.21	577.41	531.33	0.920	0.22	13.8	3.29E+05	3.03E+05	30	300000	1.10
35.03	15.55	768.34	253.55	1,037.23	24.21	394.15	371.51	0.943	0.22	13.8	2.25E+05	2.12E+05	30	300000	0.75
30.41	11.16	544.64	179.73	735.53	24.21	279.50	270.15	0.967	0.22	13.8	1.59E+05	1.54E+05	30	300000	0.53
38.95	19.53	994.51	328.19	1,342.23	24.21	510.05	472.83	0.927	0.22	13.8	2.91E+05	2.70E+05	30	300000	0.97
39.08	19.68	1,002.45	330.81	1,332.93	24.21	514.11	476.36	0.927	0.22	13.8	2.91E+05	2.72E+05	30	300000	0.98
51.15	36.57	1,930.33	637.01	2,603.93	24.21	899.48	885.28	0.895	0.22	13.8	5.64E+05	5.05E+05	30	300000	1.88
47.42	30.69	1,605.70	529.88	2,166.27	24.21	823.18	743.08	0.903	0.22	13.8	4.69E+05	4.24E+05	30	300000	1.56
29.94	10.77	524.05	172.94	707.76	24.21	268.95	260.74	0.969	0.22	13.8	1.53E+05	1.49E+05	30	300000	0.51
49.36	33.68	1,770.56	584.28	2,338.52	24.21	907.64	815.39	0.898	0.22	13.8	5.17E+05	4.65E+05	30	300000	1.72
51.66	37.42	1,977.48	652.57	2,652.57	24.21	1013.64	905.88	0.894	0.22	13.8	5.78E+05	5.16E+05	30	300000	1.93
47.80	31.27	1,637.38	549.34	2,208.98	24.21	839.41	757.00	0.902	0.22	13.8	4.78E+05	4.31E+05	30	300000	1.59
34.24	14.57	726.52	239.75	980.84	24.21	372.72	352.67	0.946	0.22	13.8	2.12E+05	2.01E+05	30	300000	0.71
<b>TOTAL</b>	<b>1.00E+03</b>	<b>52,759.05</b>	<b>1.74E+04</b>	<b>7.12E+04</b>							<b>1.54E+07</b>	<b>1.39E+07</b>			

<i>Acer rubrum</i>															
dbh	leaf mass	Tree mass (kg)			[9Be] leaf	[9Be] wood	9Be total	9Be litterfall	fraction in litterfall	10Be wood	10Be leaf	10Be total	10Be in litterfall	area	Tree inventory
(cm)	(kg)	aboveground	Below-ground	total	(mg/kg)	(mg/kg)	(mg)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at/g)	(10 <sup>6</sup> at/g)	(m <sup>2</sup> )	10 <sup>6</sup> at/yr	
10.25	1.09	36.34	11.99	49.43	19.63	0.52	25.70	21.38	0.832	0.39	14.8	1.94E+04	30	300000	0.06
0.60	14.25	.04	0.01	14.31	19.63	0.52	7.44	279.70	37.598	0.39	14.8	5.61E+03	30	300000	0.02
0.75	3.11	.08	0.03	3.21	19.63	0.52	1.67	60.98	36.561	0.39	14.8	1.26E+03	30	300000	0.00
0.95	1.07	.13	0.04	1.24	19.63	0.52	0.65	21.00	32.442	0.39	14.8	4.88E+02	30	300000	0.00
2.01	0.24	.77	0.25	1.26	19.63	0.52	0.66	4.77	7.260	0.39	14.8	4.95E+02	30	300000	0.00
1.15	0.58	.20	0.07	0.85	19.63	0.52	0.44	11.44	25.750	0.39	14.8	3.35E+02	30	300000	0.00
2.29	0.23	1.05	0.35	1.63	19.63	0.52	0.85	4.53	5.348	0.39	14.8	6.39E+02	30	300000	0.00
0.93	1.17	.12	0.04	1.34	19.63	0.52	0.70	23.02	33.082	0.39	14.8	5.25E+02	30	300000	0.00
0.89	1.39	.11	0.04	1.54	19.63	0.52	0.80	27.34	34.083	0.39	14.8	6.05E+02	30	300000	0.00
0.76	3.02	.08	0.03	3.13	19.63	0.52	1.63	59.34	36.515	0.39	14.8	1.23E+03	30	300000	0.00
0.75	3.33	.07	0.02	3.43	19.63	0.52	1.78	65.39	36.671	0.39	14.8	1.34E+03	30	300000	0.00
1.05	0.76	.16	0.05	0.98	19.63	0.52	0.51	14.99	29.323	0.39	14.8	3.85E+02	30	300000	0.00
1.09	0.68	.18	0.06	0.92	19.63	0.52	0.48	13.39	27.960	0.39	14.8	3.61E+02	30	300000	0.00
0.74	3.58	.07	0.02	3.67	19.63	0.52	1.91	70.27	36.773	0.39	14.8	1.44E+03	30	300000	0.00
0.64	8.79	.05	0.02	8.86	19.63	0.52	4.61	172.56	37.462	0.39	14.8	3.47E+03	30	300000	0.01
0.86	1.63	.10	0.03	1.77	19.63	0.52	0.68	32.02	34.816	0.39	14.8	6.93E+02	30	300000	0.00
2.04	0.24	.80	0.26	1.30	19.63	0.52	0.68	4.73	6.995	0.39	14.8	1.18E+03	30	300000	0.00
0.76	2.90	.08	0.03	3.01	19.63	0.52	1.56	56.99	36.444	0.39	14.8	5.09E+02	30	300000	0.00
2.32	0.23	1.08	0.36	1.66	19.63	0.52	0.86	4.52	5.236	0.39	14.8	6.51E+02	30	300000	0.00
1.32	0.42	.28	0.09	0.79	19.63	0.52	0.41	8.19	19.867	0.39	14.8	3.11E+02	30	300000	0.00
0.64	8.79	.05	0.02	8.86	19.63	0.52	4.61	172.56	37.462	0.39	14.8	3.47E+03	30	300000	0.01
2.02	0.24	.78	0.26	1.28	19.63	0.52	0.67	4.75	7.136	0.39	14.8	5.02E+02	30	300000	0.00
2.02	0.24	.78	0.26	1.27	19.63	0.52	0.66	4.75	7.179	0.39	14.8	4.99E+02	30	300000	0.00
0.54	32.11	.03	0.01	32.16	19.63	0.52	16.72	630.33	37.697	0.39	14.8	1.26E+04	30	300000	0.04
0.99	0.94	.14	0.05	1.13	19.63	0.52	0.59	18.37	31.361	0.39	14.8	4.42E+02	30	300000	0.00
1.04	0.79	.16	0.05	1.00	19.63	0.52	0.52	15.44	29.657	0.39	14.8	3.93E+02	30	300000	0.00
0.49	79.58	.03	0.01	79.61	19.63	0.52	41.40	1562.11	37.733	0.39	14.8	3.12E+04	30	300000	0.10
0.53	39.55	.03	0.01	39.59	19.63	0.52	20.59	776.27	37.709	0.39	14.8	1.55E+04	30	300000	0.05
1.03	0.82	.16	0.05	1.03	19.63	0.52	0.53	16.09	30.095	0.39	14.8	4.03E+02	30	300000	0.00
4.93	0.36	6.43	2.12	8.91	19.63	0.52	4.63	7.03	1.517	0.39	14.8	3.49E+03	30	300000	0.01
1.09	0.68	.18	0.06	0.92	19.63	0.52	0.48	13.27	27.845	0.39	14.8	3.59E+02	30	300000	0.00
0.94	1.13	.13	0.04	1.30	19.63	0.52	0.67	1.30	32.812	0.39	14.8	5.08E+02	30	300000	0.00
1.87	0.26	.65	0.21	1.11	19.63	0.52	0.58	5.01	8.638	0.39	14.8	4.37E+02	30	300000	0.00
1.91	0.25	.68	0.23	1.16	19.63	0.52	0.60	4.92	8.158	0.39	14.8	4.55E+02	30	300000	0.00
TOTAL	2.14E+02	52.04	1.72E+01	2.84E+02							1.11E+05	3.17E+06			

Table 5: These tables have show the data derived from the allometric equations for all trees of the four main species of trees in my field site.

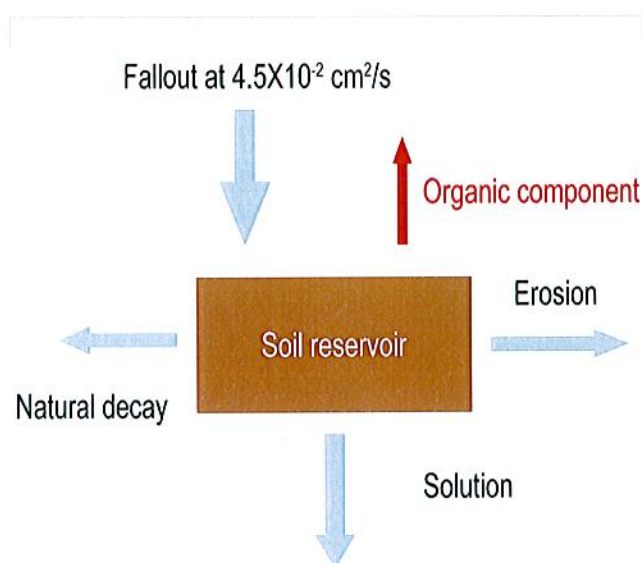


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## Appendix E: The potential role of fungus in cosmogenic beryllium cycling

### 1. Overview of fungi in the soils



*Illustration A18: This simple box model is modified from Illus. 1 to show that organic components provide a route out of the soil column. The amount of  $^{10}\text{Be}_{\text{met}}$  lost by erosion or solution is dependent on the environment. The half-life of  $^{10}\text{Be}_{\text{met}}$  is 1.4 Ma. The accumulation of  $^{10}\text{Be}_{\text{met}}$  in the system is  $4.5 \times 10^2 \text{ cm}^2/\text{s}$ .*

There are several reasons why taking a look at the role of fungus in the geochemical cycle was the next logical step. Previously, it was noted that beryllium is mobile in acidic soils with a  $\text{pH} < 5$ . Most fungi have the ability to produce a locally acidic environment to help them break down the soil into nutrients they can use (Gadd, 1999). Fungi are used in studies of soil remediation because of their ability to decompose even toxic elements. Høiland (1995) notes that while beryllium is somewhat toxic,

fungi can absorb and tolerate 7.2 to 14.4 mM (4.34 to 8.67 atoms of beryllium respectively) in the hyphae before growth is stunted. When all the previous information detailed above is taken into consideration, it is possible to modify illustration 6 to reflect another potential route out of the system through organic material (illustration 11).

Fungi can play an important role in sequestering both  $^{10}\text{Be}$  and  $^9\text{Be}$ . Fungi produce chelants and create a localized acidic environment which chelates the beryllium in the soil (Goodell, 1997). This draws the beryllium out of the soils allows for the beryllium species to adsorb to organic matter or be absorbed by the fungi (Gadd, 1999; Høiland,

1995). It has been consistently shown that live wood contains considerably less  $^{10}\text{Be}$  than dead wood (Barg et al., 1997; Lundberg et al., 1983), implying that the fungus living on the wood may concentrate the beryllium. Furthermore, fungi may also alter the leaf and wood chemistry to bind to metals better (Filley, 2002, 2003).

Fungi absorb nutrients and minerals from the soil indiscriminately and keep a cache of the nutrients and minerals for later use. Fungi will eventually excrete what it does not need after it fruits into the surrounding material, such as wood. Beryllium is not an essential component of the fungi diet, so it is excreted and left behind when the body of the fungus dies (Kendrick, 2000). This cache of beryllium can alter the data, but to what degree? It has been shown that up to 8.67 mM of total beryllium can be sequestered in the fungus (Høiland, 1995). To know how this translate to an age or erosion rate, the [ $^{10}\text{Be}$ ] must be accounted for through quantitative measurements.

We suggest that  $^{10}\text{Be}$  is mobilised by fungi in soils, which have implications for the reliability of  $^{10}\text{Be}$  as an erosion tracer. This study was designed to take a closer look at the quantity of beryllium in soils that is transported and held by the fungus *Ganoderma tsugae*, as well as how much of this beryllium is deposited in the wood the fungi resides and dies in.

## 2 Sampling methods

The following study is a coarse experiment aimed at scratching the surface of the role of fungus in the  $^{10}\text{Be}_{\text{met}}$  geochemical cycle. For that reason, we chose to sample material from places that were convenient and easy to obtain. This is by no means a conclusive study, and much more work needs to be done for a definitive answer on fungi's role within the cosmogenic beryllium geochemical cycle.

### Fungus

The fungus used for this analysis, *Ganoderma tsugae*, came from Woodruff, Wisconsin. It was obtained by Brian Schwingle of Wisconsin's Department of Natural

Resources, and shipped to Purdue University. Schwingle included two chunks of hemlock wood; a large, piece with a *G. tsugae* growing from it, and a smaller piece with evidence of manganese deposits in it, but no fungal growth protruding from the smaller piece of wood.

There are two primary reasons why *G. tsugae* was used. 1.) Cosmogenic beryllium accumulates with manganese nodules on the ocean floor (Somayajulu, 1967), and *G. tsugae* is a fungus that is known to leave behind visible black flecks that contain a high concentration of manganese. It stands to reason that there is a good chance that  $^{10}\text{Be}_{\text{met}}$  may accumulate in the manganese-rich flecks left behind by the fungal hyphae as it deposits unused nutrients in the wood. 2.) The sample was easily obtained and generously sent to us by Brian Schwingle of Wisconsin's Department of Natural Resources.

#### Decayed and non-decayed wood

In addition an exploratory analysis of chunks of the decayed and non-decayed wood used in this experiment was from a wooded area on a glacial terrace west of Purdue University campus. These pieces of wood samples were cut from trees or stumps that were partially decayed. A sample pieces of decayed and non-decayed wood was taken from the same tree or stump.

#### 3 Sample digestion and beryllium chemistry

Sample digestion of the both the fungus and the wood samples were done similarly to that of the wood, leaf, and nuts samples, as described in chapter two, section 2.3. The sample digestion is a modified from a protocol used by the National Soil Erosion Lab to dissolve organic soils. A detailed, step by step protocol can be found in Appendix C.

The wood and fungi samples were dried at 70°C overnight and massed. For chemical digestion, the samples were first ashed in an open nickel crucible over a Bunsen

burner. I estimated the temperature of the crucible to be about 900°C (bright orange) for a majority of the burning process, which lasted 30-45 minutes. For the final 2 minutes of ashing, the gas was turned up so that the crucible turned white hot to burn away any left over organics, leaving only white ash behind. The ash was massed, then dissolved in an acid bomb with HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, at 200°C for 6 hours before cooled and moved into Teflon beakers for the next step.

The remaining material was alternately fumed in H<sub>2</sub>SO<sub>4</sub> and HCl until total digestion had occurred. The samples sometimes contained silica that did not dissolve in these acids; these were treated with hydrofluoric acid and then fumed in sulfuric acid to drive away any fluorides.

Following digestion and drydown, the samples were dissolved in 1:1 HCl, and an aliquot taken for elemental analysis by ICP-OES. The remaining sample was spiked with <sup>9</sup>Be, and beryllium was isolated for AMS using standard methodologies as explained in chapter 2, section 2.3.5.

#### 4 Results

The samples were run on an auto-sampling ICP-OES. The data obtained was for 26 elements in the parts per million (ppm) range, given in illus. 2.

While the OES gives the ppm of individual elements, it does not give the amount of <sup>10</sup>Be<sub>met</sub> in the samples. The samples associated with the tree section from Wisconsin were normalised against the bulk tree, the oak samples against non-decayed oak, and decayed hickory against non-decayed hickory. Of these 26 elements, aluminium, titanium, chromium, and manganese were enriched in almost all of the samples (Illus. 2). The AMS data has been plotted on these graphs to show the relative enrichment of the <sup>10</sup>Be. Hickory showed a possible loss of <sup>10</sup>Be, while the rest of the samples show consistency with accumulation from rain water.

Using the same models as section 2.4.1, we can now calculate the transfer factors ( $T_{\text{fungus}}$ ) for the fungus. In section 2.4.1, we calculated the transfer factors as a ratio of

beryllium at the surface of the soil. However, with this experiment we had the decayed wood and non-decayed wood. The ratios were calculated relative to the beryllium in the non-decayed wood (decayed/non-decayed) for the wood samples. In the case of the *G. tsuugae* fruiting body and manganese splinters, they were calculated with the bulk wood the fruiting body was growing on and the Mn was deposited in. This is represented in illustration 3 and summarized in table 1.

### 5 Conclusions

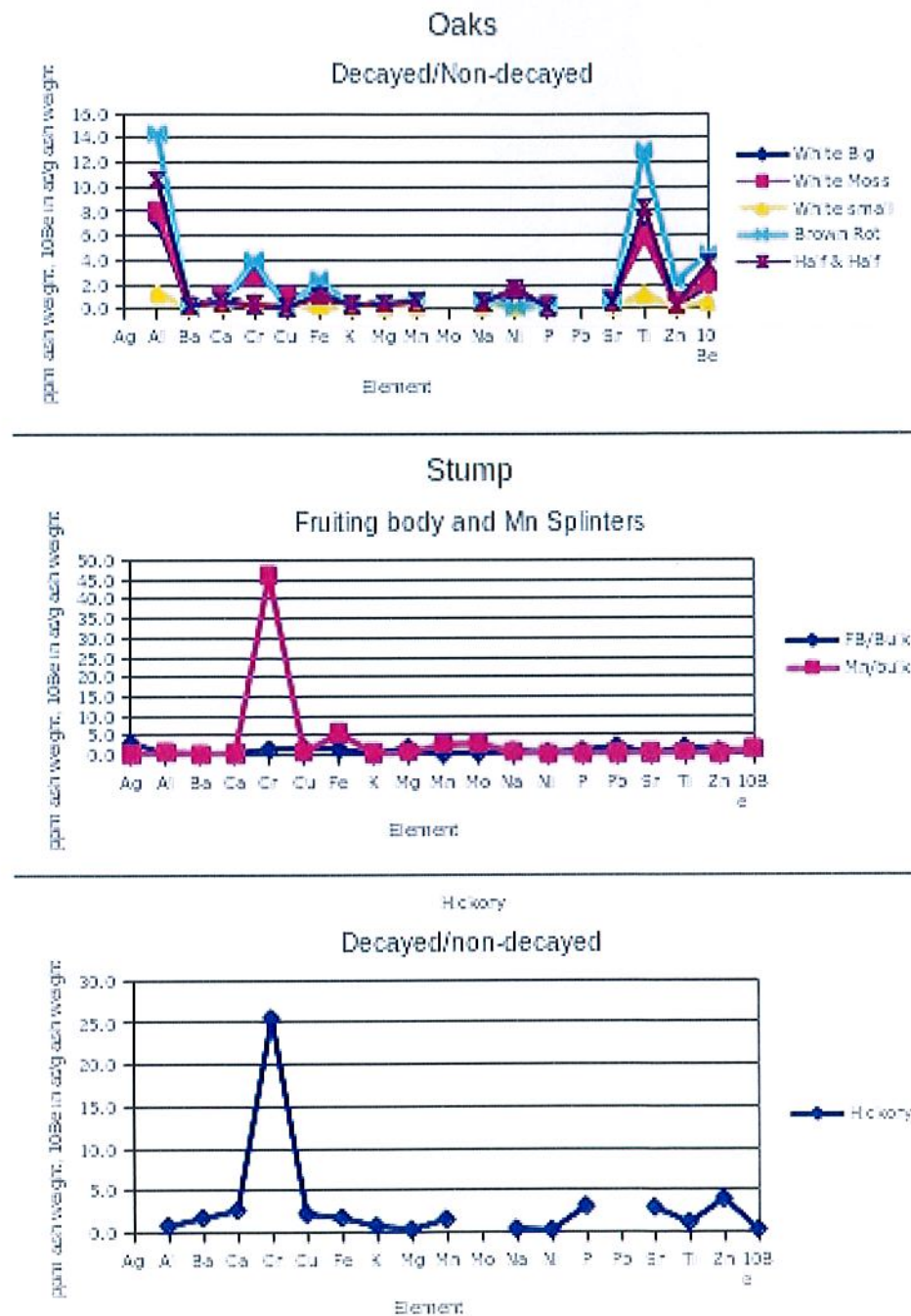
From these data we reached two conclusions: Oak has a  $^{10}\text{Be}_{\text{met}}$  concentration of about  $2 \times 10^6$  atoms/g, similar to that observed by Klein et al. (1982). Hickory has a significantly higher concentration of about  $3 \times 10^7$  atoms/g, confirming observations that hickory bioaccumulates beryllium. Using these data, the inventory of  $^{10}\text{Be}_{\text{met}}$  in a temperate forest is expected to be about  $6 \times 10^6$  atoms/cm<sup>2</sup>, which matches what we calculated earlier in chapter 2. This is equivalent to only a few years of fallout.

We observed two patterns of metal accumulation by wood-degrading fungi. One group of samples showed enrichment in Mn, Fe, and Cr, which are metals that can be used for energy by fungi in a Fenton-like process. This group showed no enrichment in  $^{10}\text{Be}_{\text{met}}$ . Another group of samples showed enrichment primarily in Al and Ti, and also five-fold enrichment in  $^{10}\text{Be}_{\text{met}}$ . Neither group showed fungal enrichment of  $^{10}\text{Be}_{\text{met}}$  sufficient to account for the 1000-fold difference between living trees and soil organic matter.

It is not precisely clear whether the fungi is acting as an agent of transport or not. The enrichment in the decayed wood could potentially be a reflection of rainfall depending on the amount of time the tree has been decaying, while chromium and iron are possibly being used as oxidisers.

Element	Fruiting Body	Tree Bulk	Mn Splinters	Non-decayed hickory	Decayed Hickory	Non-decayed Birch	White Big	White Moss	White small	Brown Rot	Half & Half	Non-decayed Oak
Ag	76.4	25.5	7.1	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0	88.0
Al	2339.1	3186.2	2415.8	454.9	355.4	1878.1	5632.8	6178.4	1026.3	11112.0	8187.9	774.4
Ba	94.8	891.9	142.1	305.4	526.0	623.5	154.1	47.6	49.5	200.0	211.6	651.2
Ca	29658.9	287945.6	102317.2	37039.3	97380.3	34556.8	166829.6	190594.3	42042.4	98897.1	98439.2	169083.2
Cr	36.7	28.0	1293.2	1.9	49.8	15.0	21.5	142.9	37.1	211.1	18.4	52.8
Cu	366.9	203.9	113.7	32.5	71.1	225.4	89.5	365.3	24.7	22.2	55.2	334.4
Fe	1253.6	942.8	5186.9	175.4	298.5	262.9	3081.5	4733.1	754.3	7889.5	3496.0	3273.6
K	40360.5	178373.4	71053.6	41587.9	29853.8	51084.0	17163.4	25889.1	5440.8	17779.3	23919.8	62339.2
Mg	21403.3	12231.3	8029.1	22743.4	7108.1	4582.5	11812.3	7464.9	1854.8	12223.2	10119.9	23302.4
Mn	2033.3	25991.6	64658.8	1949.4	2985.4	2629.3	2551.3	1572.4	457.5	3111.4	2392.0	3872.0
Mo	1.5	5.1	14.2	0.0	0.0	0.0	0.0	6.4	0.0	0.0	0.0	0.0
Na	1528.8	1783.7	1023.2	2664.2	924.0	1652.7	1192.8	1651.8	284.4	2222.4	1472.0	2728.0
Ni	3760.9	7262.3	540.0	4158.8	710.8	10066.5	281.6	2827.1	321.5	422.3	4784.0	2921.6
P	31799.2	33126.5	4050.1	1429.6	4407.0	2779.6	2766.7	3017.7	445.2	3667.0	1380.0	8307.2
Pb	55.0	25.5	7.1	0.0	0.0	0.0	12.6	0.0	0.0	0.0	0.0	0.0
Sr	76.4	611.6	298.4	117.0	334.1	262.9	241.9	254.1	61.8	222.2	156.4	281.6
Ti	91.7	51.0	28.4	19.5	21.3	30.0	465.5	428.8	86.6	933.4	598.0	72.2
Zn	626.8	688.0	149.2	175.4	689.5	300.5	104.4	270.0	43.3	1089.0	119.6	492.8
<sup>10</sup> Be	54.86	51.43	76.32	969.62	256.62	39.96	326.70	371.85	99.42	775.53	633.19	173.34

Table A6: This table shows the ICP-OES data of all samples across all elements, plus <sup>10</sup>Be<sub>meq</sub>.



*Illustration A19: Three graphs showing all the elements transfer factors from the OES calculated as decayed/non-decayed.  $^{10}\text{Be}_{\text{ref}}$  is on the far right of the graph to show relative relationship to other elements in the wood, fruiting body and Mn splinters.*



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