# Analysis of Lead Isotopes in *Quercus alba*, *Liquidamber stryaciflua*, and *Pinus taeda* as a Metric for Pollutant Contributions From Air Transportation

Samuel L. Kane, Lauren Finch, Margot J. Hillyer, Michael C. Leopold, and Todd R. Lookingbill


## Abstract

Lead as a component of aviation grade gasoline can have a detrimental effect on tree health. Early deaths as well as the returning of lead to the water table via decomposition presents environmental hazards for communities and ecosystems. This study compared three different tree species (*Quercus alba, Liquidamber stryaciflua,* and *Pinus taeda )* collected from Richmond International Airport in Richmond, Virginia for lead content. Trees were cored and these samples were then digested into a clear liquid with a Digestdahl Digestion Apparatus, tested with a Varian AA 240ZZ graphite furnace atomic spectroscopy. When compared to control values there was there was no statistically significant difference between them and experimental core values (P-value of 0.4537). These results suggest that the pollution of lead due to aircraft is minimally or not affecting the accumulation of sequestered lead. Additionally, an investigation was conducted to investigate the difference in accumulation of lead in differing tree species. There was a statistically significant difference in the accumulation of lead in oak trees when compared to pines tree and nearly significant in pine trees when compared to sweet gums (P-values of 0.0045 and 0.0698 respectively). This work has implications for determine the effects of air transportation on the surrounding environment.


## Introduction

Lead is a commonly known heavy metal that has been linked to multiple ailments such as difficulties in concentration, learning disabilities, and adverse effects on the cardiovascular system and blood chemistry. A blood lead level (BLL) of 45µL/dL is the current maximum limitation for when medical treatment is a must with 10µL/dL being the level where medical treatment is advised to prevent any damage from occurring. The air transportation industry is one of the largest remaining contributors to atmospheric lead pollution with current aviation gasoline having 2.42g/L. Tree species are known to sequester lead sources though multiple means, the most effective being waterborne lead uptake though the root system; with alternative pathways available though leave absorption from both airborne and waterborne lead and though bark absorption. Lead within tree xylem behaves in an immobile and mobile form. Lighter lead compounds stay concentrated towards the outer five rings while heavier compounds stay behind, this promotes the idea of dendrochronology as an effective mean of measuring lead concentrations in historic times as well as in recent years however limits the comparability on a general level between old and new growth tree ring sections. Differing growth patterns are thought to be a possible varying factor between tree species as well as distance from a lead source is thought to vary the concentration of lead within a tree. These two factors were the target goals of the study.

A)

B)

C)

D)

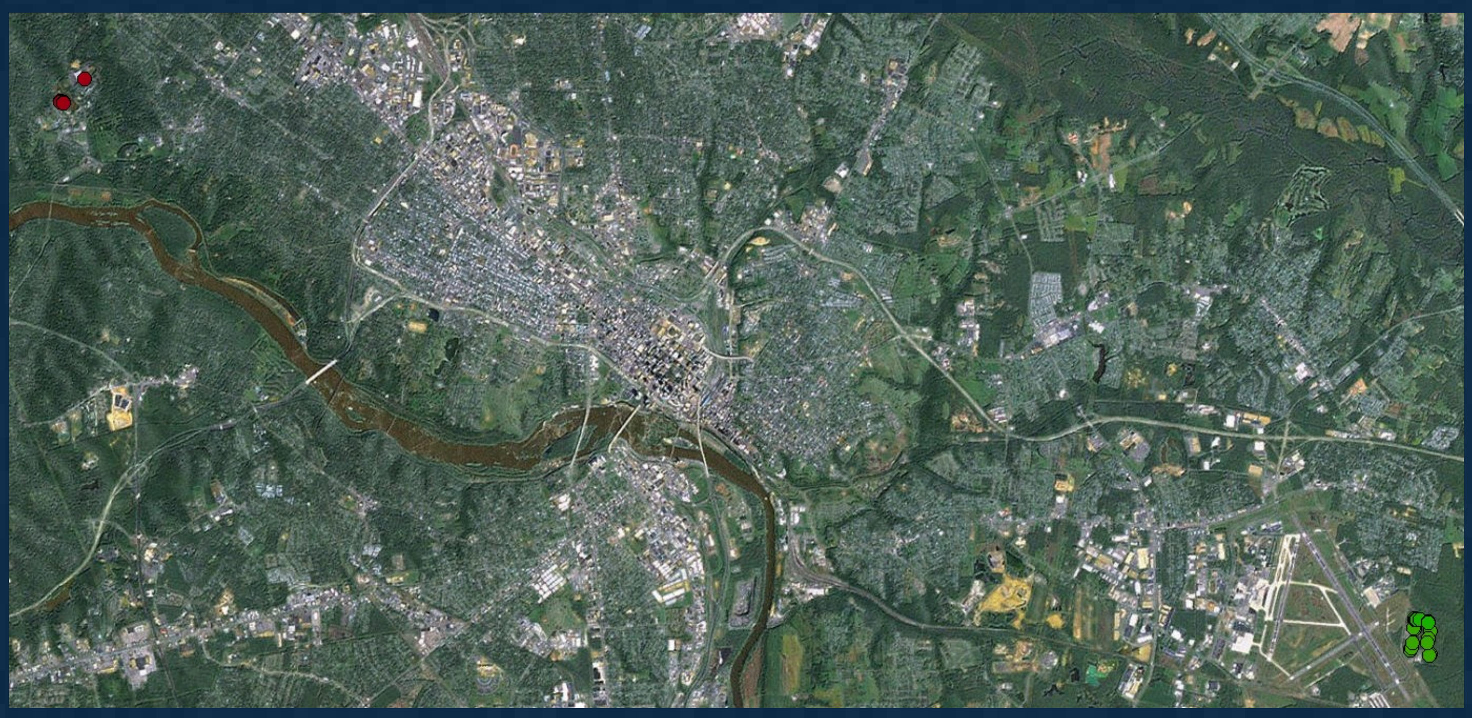
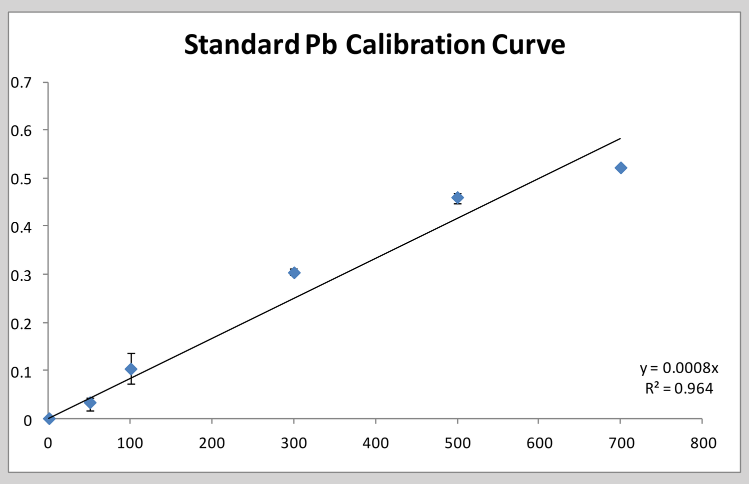


Figure 1— a) Areal view of the control sites at University of Richmond in the Westhampton Forest b) Areal view of the experimental sites at Mullin's National Guard Armory c) Proximity of Richmond International Airport to the experimental site d) Areal view of the entire study area highlighting the distance between control and experimental sites

## Results




| Lead Concentration (ppb) | Absorbance Value 1 | Absorbance Value 2 | Absorbance Value 3 | Average Absorbance | Upper Error | Lower Error |
|---|---|---|---|---|---|---|
| 0 | 0.0008 | 0.0003 | 0.0007 | 0.0006 | 0.0002 | 0.0003 |
| 50 | 0.0161 | 0.0414 | 0.044 | 0.033833 | 0.010167 | 0.017733 |
| 100 | 0.0717 | 0.1044 | 0.1353 | 0.1038 | 0.0315 | 0.0321 |
| 300 | 0.2997 | 0.2997 | 0.3131 | 0.304167 | 0.008933 | 0.004467 |
| 500 | 0.4682 | 0.4472 | 0.4665 | 0.460633 | 0.007567 | 0.013433 |
| 700 | 0.5219 | 0.525 | 0.5207 | 0.522533 | 0.002467 | 0.001833 |

| ID | Tree Species | Mass (g) | Absorbance Value (AU) | Lead Value (ppb/g) |
|---|---|---|---|---|
| Control 1-2 | Oak | 0.275 | 0.069 | 23.71875 |
| Control 1-5 | Oak | 0.2609 | 0.412 | 134.3635 |
| Control 2-1 | Pine | 0.2409 | 0.2653 | 79.88846 |
| Control 3-1 | Sweet | 0.2347 | 0.169 | 49.58038 |
| Control 5-1 | Oak | 0.261 | 0.0854 | 27.86175 |
| Experimental 1-1 | Pine | 0.2174 | 0.0409 | 11.11458 |
| Experimental 1-2 | Pine | 0.2141 | 0.0121 | 3.238263 |
| Experimental 1-3 | Pine | 0.2846 | 0.0453 | 16.11548 |
| Experimental 2-1 | Oak | 0.2555 | 0.2218 | 70.83738 |
| Experimental 3-1 | Sweet | 0.2955 | 0.2799 | 103.3881 |
| Experimental 3-2 | Sweet | 0.2691 | 0.1859 | 62.53211 |
| Experimental 4-1 | Pine | 0.2948 | 0.102 | 37.587 |
| Experimental 5-3 | Oak | 0.2594 | 0.1626 | 52.72305 |
| Experimental 6-1 | Pine | 0.2925 | 0.1091 | 39.88969 |
| Experimental 6-2 | Pine | 0.3063 | 0.1839 | 70.41071 |
| Experimental 6-3 | Pine | 0.3001 | 0.1553 | 58.25691 |
| Experimental 7-1 | Pine | 0.3011 | 0.0961 | 36.16964 |
| Experimental 7-2 | Pine | 0.3269 | 0.1001 | 40.90336 |
| Experimental 8-1 | Oak | 0.4769 | 0.256 | 152.608 |
| Experimental 8-2 | Oak | 0.2635 | 0.4275 | 140.8078 |
| Experimental 8-3 | Oak | 0.2792 | 0.1684 | 58.7716 |
| Experimental 10 | Oak | 0.8515 | 0.072 | 29.547 |
| Experimental 11 | Pine | 0.7385 | 0.0913 | 29.216 |
| Experimental 12 | Oak | 1.4334 | 0.1722 | 106.3981 |
| Experimental 13 | Pine | 0.942 | 0.0892 | 33.52805 |
| Experimental 14 | Oak | 1.2054 | 0.1007 | 56.83256 |
| Experimental 17 | Pine | 0.9111 | 0.2894 | 113.9513 |
| Experimental 19 | Pine | 0.8352 | 0.3146 | 100.0821 |
| Experimental 20 | Oak | 1.4521 | 0.2338 | 141.0399 |
| Experimental 21 | Pine | 0.856 | 0.149 | 51.49813 |
| Experimental 22 | Oak | 1.0121 | 0.1421 | 84.99356 |

| Tree Type | Average (All Values) | Average (Control) | Average (Experimental) |
|---|---|---|---|
| Oak | 83.11561 | 48.12331 | 71.83352 |
| Pine | 61.98133 | 79.88846 | 49.58038 |
| Sweet Gum | 89.45589 | 45.85437 | 82.96009 |

| Test Type | One Tailed P-value | Two Tailed P-value |
|---|---|---|
| Control vs. Experimental | 0.453713 | 0.907426 |
| Oak vs. Pine (Experimental) | 0.004542 | 0.009084 |
| Oak vs. Sweet Gum (Experimental) | 0.42304 | 0.846079 |
| Pine vs. Sweet Gum (Experimental) | 0.069863 | 0.139725 |

| Set Type for Comparison | P-value |
|---|---|
| All Values | 0.07242 |
| Control Values | 0.94381 |
| Experimental Values | 0.023918 |

## Discussion

ANOVA Single Factor tests and t-test comparison assuming equal variances reveal multiple conclusions about the relationships between distance and tree species. Over any distance there seems to be no statistically significant differences between the values of lead found in trees (P-value of 0.4537). This suggests that regardless of the location of a sampled tree within a buffer of 40km centered at the airport, the average lead content of that tree will be approximately the same. On a smaller scale however, results show that there is a statistically significant difference in lead concentration between experimental tree species but not between control tree species (P-values of 0.0239 and 0.9438 respectively). Because of this difference lead concentration values are different between species of trees located close to airports but not between species of trees located further away. When comparing experimental lead concentration values between tree species Oak trees were statistically significantly different versus Pine trees but not Sweet Gum trees (P-values of 0.0045 and 0.4230 respectively); Pine trees were nearly statistically significantly different from Sweet Gums with a P-value of 0.0698 which suggests a possible relationship). In relation to the initial hypothesis, results show no difference in mean lead concentrations in trees over distance. However when comparing tree species, results show that mean lead concentrations further away from an airport would be closer together where as mean lead concentration values closer to the airport would vary more but have the same total area mean (the mean lead concentration value for a space regardless of species) as trees further away. The applications of this research can be found in determining the effects of the air transportation industry on lead concentrations in surround trees and can be applied when planning for large area clear cutting of tree species and the subsequent cleanup by giving a prioritization for which trees should be prioritized and what areas are most at risk of having a higher lead concentrations. In conclusion, the effects of air transportation on total area mean is not significant over a distance of less than 40km however the relative concentrations of lead within differing tree species in a small region (<1km) showed high variability suggesting a per species specific mean lead concentration. Further work can be done into the exploration of different tree species, different heavy metal and pollutant levels, and different industry.

## Methodology

-Sample Collection-

Samples sites were chosen using a nonaligned block design, in which 22 points were randomly located with 70m cells defined by the site access road.. Transect lines are approximately 70m apart. Trees are selected by target species which filled the following roles: Slow growing hardwood, fast growing softwood, or evergreen (*Quercus alba, Liquidamber stryaciflua,* and *Pinus taeda respectively)* and must meet a minimum diameter at breast height measurement of 20cm. Due to ecological constraints, all selected sites only have two trees collected because the third species could not be found within a reasonable distance (10—15m). Using an increment borer placed at chest height three samples were extracted from each tree from multiple directions. Cores were then placed into plastic straws with tape labeling them with the following information: Experimental ID, Common name of the tree, vertex of collection, sample number date, and collector. Upon returning to the lab, samples were stored in a freezer to prevent molding.

-Sample Digestion-

Using a razor blade, samples were removed from their straws and the outermost ring and bark were removed before cutting the sample mass between 0.2500g. And 0.5000g from the outermost ring inward. The samples were then transferred into labeled glass scintillation vials and dried in an oven at 70°C for at least 24 hours. The dried samples were then placed into a 100mL glass volumetric flask and digested using the Hach Digestdahl Digestion Apparatus according to standard procedure for Piranha solution. Samples in 100mL volumetric flasks are treated with 4.0mL of concentrated sulfuric acid. After the solution darkens, the acid solution was inserted into the digestion apparatus and heated to 440°C before 50% (wt) $H_2O_2$ was slowly metered into the reaction. Metering of $H_2O_2$ continued until the digest turned clear taking care not to evaporate the digest to dryness. The sample digest was then allowed to cool before being transferred to a small volumetric flask, where it was then labeled with the Experimental ID and Sample ID. Samples are then placed into cold storage (7°C) to keep samples. Samples 10—22 were combined to produce a tri-core sample and then pre-digested using concentrated sulfuric acid and 30% (wt) $H_2O_2$ dropwise until the sample was translucent and golden in color.

-Sample Analysis-

For the quantification of lead, sample were taken out of cold storage and analyzed with a Varian AA 240Z graphite furnace atomic absorption spectrophotometer featuring an auto sampler using a hollow cathode lamp source (283.3 nm, 10 mA). The temperature profile in use by the furnace included a 85-120°C preconditioning step followed by an increase in temperature to 400°C briefly before being increased again to 800°C and then ramped up to 2500°C.

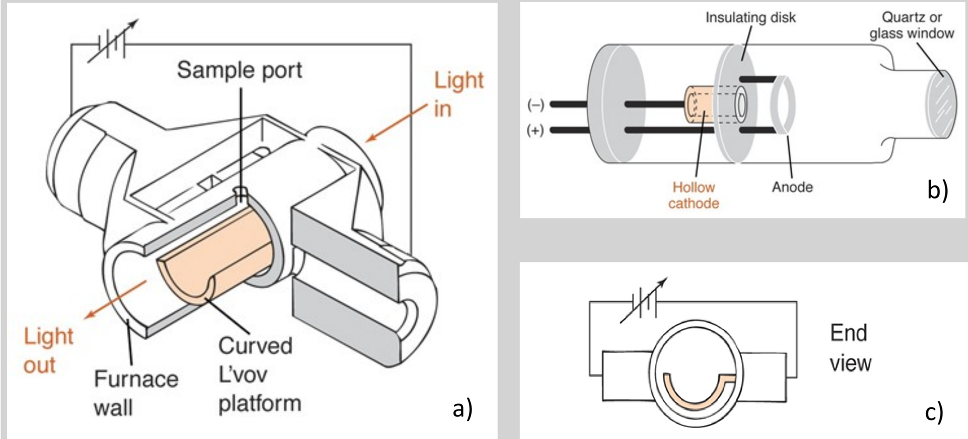



Figure 2— a) A cut-away depiction of the interior of a graphite furnace with furnace tube in place. b) A x-ray depiction of the inner construction of a hallow cathode tube. b) The end view of a graphite furnace showing the L'vov platform's positioning.

-Statistical Analysis-

ANOVA single factor tests were used to compare the three species of trees at both of the sites. T-tests were used to compare each to the average lead value of each site along with the average of each genera of tree.


## Acknowledgements

This work is supported by Commonwealth Health Research Board and the Camille & Henry Dreyfus Foundation's Henry Dreyfus Teacher-Scholar Award. SLK and LEF or MMH were supported by the Howard Hughes Medical Institute and the Chemistry Department's Puryear-Topham Fund, respectively.


## References


Abrams, M. D., & Sands, B. A. (2010). Oak Forest Composition on Contrasting Soil Types at the Mohonk Preserve, Eastern New York.*Northern Journal of Applied Forestry*, *27*(3), 105–109. Retrieved fromhttp://www.ingentaconnect.com/content/saf/njaf/2010/00000027/00000003/art00004

Amani, H. S., Hashemi, S. A., & Torabian, S. Y. (2013). Studying the Reaction of Long Oak Apple Trees to the Absorption of Lead in the Industrial Park of Rasht. *Journal of Agricultural & Biological Science*,*8*(2), 97–100.

Center for History and New Media. (n.d.). Zotero Quick Start Guide. Retrieved from http://zotero.org/support/quick_start_guide

Donovan, L. A., West, J. B., & McLeod, K. W. (2000). Quercus species differ in water and nutrient characteristics in a resource-limited fall-line sandhill habitat. *Tree Physiology*, *20*(14), 929–936.

Hagemeyer, J., & Weinand, T. (1996). Radial distributions of Pb in stems of young Norway spruce trees grown in Pb-contaminated soil. *Tree Physiology*, *16*(6), 591–594.

Marcantonio, F., Flowers, G., Thien, L., & Ellgaard, E. (1998). Lead Isotopes in Tree Rings: Chronology of Pollution in Bayou Trepagnier, Louisiana.*Environmental Science & Technology*, *32*(16), 2371–2376. doi:10.1021/es980109v

Marguí, E., Iglesias, M., Queralt, I., & Hidalgo, M. (2006). Lead isotope ratio measurements by ICP-QMS to identify metal accumulation in vegetation specimens growing in mining environments. *Science of The Total Environment*, *367*(2–3), 988–998. doi:10.1016/j.scitotenv.2006.03.036

Nabais, C., Freitas, H., & Hagemeyer, J. (1999). Dendroanalysis: a tool for biomonitoring environmental pollution? *Science of The Total Environment*, *232*(1–2), 33–37. doi:10.1016/S0048-9697(99)00107-2

Patrick, G. J., & Farmer, J. G. (2006). A stable lead isotopic investigation of the use of sycamore tree rings as a historical biomonitor of environmental lead contamination. *Science of The Total Environment*,*362*(1–3), 278–291. doi:10.1016/j.scitotenv.2005.12.004

Patrick, G. J., & Farmer, J. G. (2007). A lead isotopic assessment of tree bark as a biomonitor of contemporary atmospheric lead. *Science of The Total Environment*, *388*(1–3), 343–356. doi:10.1016/j.scitotenv.2007.07.047

Salma, I., Maenhaut, W., Dubtsov, S., Zemplén-Papp, É., & Záray, G. (2000). Impact of phase out of leaded gasoline on the air quality in Budapest. *Microchemical Journal*, *67*(1–3), 127–133. doi:10.1016/S0026-265X(00)00108-9

Thomas, V. M., Socolow, R. H., Fanelli, J. J., & Spiro, T. G. (1999). Effects of Reducing Lead in Gasoline: An Analysis of the International Experience. *Environmental Science & Technology*, *33*(22), 3942–3948. doi:10.1021/es990231+

Tomašević, M., Antanasijević, D., Aničić, M., Deljanin, I., Perić-Grujić, A., & Ristić, M. (2013). Lead concentrations and isotope ratios in urban tree leaves. *Ecological Indicators*, *24*, 504–509. doi:10.1016/j.ecolind.2012.08.007

Tree_Air_Qual.pdf. (n.d.). Retrieved fromhttp://www.nrs.fs.fed.us/units/urban/local-resources/downloads/Tree_Air_Qual.pdf

Watmough, S. A., & Hutchinson, T. C. (2002). Historical changes in lead concentrations in tree-rings of sycamore, oak and Scots pine in north-west England. *Science of The Total Environment*, *293*(1–3), 85–96. doi:10.1016/S0048-9697(01)01149-4