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Examination of Environmental Trends in Hawai`i Based on Trace Element Distributions in Cores of the Kiawe Tree (*Prosopis pallida)*

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INTRODUCTION

Annual growth rings of trees have a potential for providing a chronology of bioavailable contaminants extant in the environment in which the trees grow. Recent studies have documented a significant correlation between concentrations of metals in atmospheric particulate matter and those observed in surface and groundwater. The Kiawe (*Prosopis pallida*), a common hardwood tree in Hawai`i, represents a potential environmental tape recorder because of its life span on the order of multiple decades. The Kiawe is phreatophytic and has high transpiration rates, it may therefore be ideally suited to examine past (temporal) and current (spatial) variability in the quality of groundwater where the trees grow. Because of a potential correlation between airborne and groundwater pollution we hypothesize that growth rings of Kiawe may yield clues to help unravel recent (50-100 yrs) changes in environmental contamination patterns in Hawai`i.

Polynesians first sailed in voyaging canoes to the islands of Hawai`i from the South Pacific, perhaps as early as 2000 years ago. They brought with them knowledge gathered over many centuries of living on small islands across the Pacific Ocean. The first *Kanaka Maoli* (Hawaiians) knew how to preserve natural resources and create what they needed from limited amounts of land and from the sea. Kanaka Maoli cultivators and fishermen were careful observers of their environment and understood the need to conserve resources for themselves and for their children. They cared for their resources and created conditions that made them productive.

The principal site of our study, Makua valley, is located on the island of O`ahu (see maps at bottom center of the poster). Although characterized by large elevation gradients (0-1300 m), a location in the lee of the Waianae mountain range results in relatively low annual rainfall (~400 to 600 mm/yr) and sparse fresh water resources in Makua Valley. The presence of multiple temples and fishing shrines, however, attests to inhabitation of the valley and intense involvement by native Hawaiian people. With the introduction by western traders of a market economy in the late 1700s and subsequent changes to land tenure in Hawai`i during the mid-1800s, commercial values began to infiltrate Hawaiian society. Beginning around 1930, Makua Valley became a military training site and activities there since WWII have raised public concern about destruction of cultural resources and the potential for contamination of natural resources.

In this study we present preliminary results of analyses of trace elements in Kiawe wood collected from Makua valley and a site on the North Shore of O`ahu initially thought to be relatively free of significant anthropogenic inputs, particularly those associated with explosive ordnance. Because of the preliminary nature of this study we describe mostly the methodology and only briefly discuss trace element concentrations in two tree cores.





A) Acquisition of Cores from Kiawe Trees: Cores were obtained using an electric coring drill powered by a gasoline generator as shown. The top left image shows a technician drilling a Kiawe tree in Makua Valley. Cores were drilled through the entire tree from south to north, yielding cores from ~20 cm to >40 cm (top middle image). The top right image shows a slab of Kiawe wood sawed from a dead tree in Makua Valley and illustrates its irregular growth banding. The metal liner from the corer is shown in the bottom left image and a small (~20 cm) Kiawe core is shown in the bottom right image after its extrusion from the liner. Cores were placed in Saran wrap, labelled, photographed, orientation recorded and placed in plastic zip-type bags. All samples were then stored in a freezer after return to the laboratory to minimize any subsequent biological activity (e.g., growth of molds).

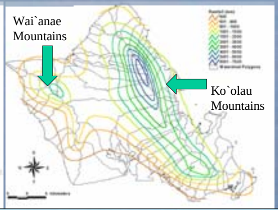
B) Sample Processing: Because the focus of this study is determining trace elements, using metallic corers potentially contaminates our samples, while also inducing frictional "burning" of the wood (top image). This outer (contaminated) layer of cores must therefore be removed prior to marking cores for subsampling (bottom image). Individual annual growth bands of Kiawe are also not always clearly discernible, hence we elected to sample at one centimeter intervals, corresponding approximately to the average (diameter) growth rate for *Prosopis sp.* (See table below). Therefore each 0.5 cm interval of the core corresponds to about one year's (radial) growth and one centimeter intervals correspond to a temporal resolution of approximately two years.


Species	Growth Rate (mm/yr)	Age and Diameter	Rainfall	Location
Honey Mesquite (P. glandulosa)	12.95 mm/yr	Not Available	Wet year	San Angelo, Texas
Honey Mesquite (P. glandulosa)	7.11 mm/yr	Not Available	Dry Year	San Angelo, Texas
Kiawe (P. pallida)	8.74-14.86 mm/yr	70 yrs old = 0.61-1.04m	940mm/yr	Punahou School, O`ahu, Hawai`i
Kiawe (P. pallida)	11.90-17.14 mm/yr	21 yrs old = 0.25-0.36m	760mm/yr	Puerto Rico
Kiawe (P. pallida)	11.25 mm/yr	88 yrs old = 0.99m		Honolulu, O`ahu, Hawai`i
Average	**12 mm/yr**			

C) Sample Processing (cont.) All sample processing was conducted in a Class 100 laminar flow bench (top image). The use of metallic tools (above left), however, was unavoidable. Clean stainless steel blades were used to the extent possible to saw cores into one centimeter sections. Each sample was subsequently "shaved" down using a small plane and ceramic knives and fragments/shavings were transferred to HCl washed Petri dishes (above right) for drying and storage prior to acid digestion.



D) Sample Preparation: Samples of a test core were digested with various reagent mixtures to evaluate trace element extraction efficiencies and to determine the range of concentrations that might be expected in other wood samples. Shavings from the core were microwave digested in sealed Teflon vessels with a series of mixtures of H_2O_2 and HNO_3. The mixtures produced similar concentration values for Co, Cu, and Mn. Concentrations of other elements (e.g., Cr, Pb, V, and Zn) varied between treatments suggesting either incomplete recovery depending on the treatment, or in some cases contamination by one reagent. Analysis of procedural blanks by TIMS showed that trace element grade H_2O_2 contained about 31 pg Pb/g. The latter is unacceptable for the TIMS analyses to determine the Pb isotopic composition. Our quartz distilled HNO_3, however, contained about 1.2 pg Pb/g, and is suitable for TIMS work.We finally settled on using only 3 mL of HNO_3 for digestion of about 250 mg of wood flakes. Resultant solutions were subsequently diluted with 0.3 M HNO_3 to a known mass and analyzed by ICP-MS using a VG-PQ2S instrument. Calibration was performed with dilutions of commercially obtained multi element standards. Accuracy of digestion procedures and analysis was ascertained by concurrently processing and analyzing NIST standard reference material 1575a (Pine Needles).

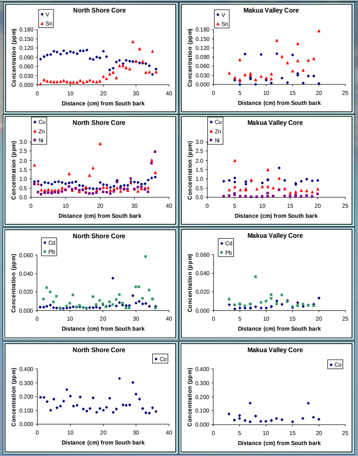


Site Location Maps Left panel: Locations of Makua Valley (green) and North Shore Kiawe tree (Red dot). Other samples (not presented in this poster) have been collected at the locations indicated by the green dots The right panel shows the distribution of annual rainfall on O'ahu. Although the peak of the Wai`anae range reaches about 250 m higher than the peak of the Ko'olau, rainfall is less than one third that of peak rainfall over the Ko`olau because predominating NE trade winds deliver most of their water content to the latter.

E) Results of ICP-MS Analysis: Results of analysis of NIST SRM 1575a (pine needles) are shown below, along with the certified, reference, or information values provided by NIST. Although the matrix of pine needles is somewhat different from that of hardwood, this NIST SRM provides the most similar matrix to our samples.

NIST 1575a		Found	Certified	Std. Error
		All Concentrations in µg/g		
Vanadium	V 51	0.146		
Chromium	Cr 52	0.456	0.3-0.5	Info. Only
Cobalt	Co 59	0.055	0.061	0.002
Nickel	Ni 60	1.54	1.47	0.10
Nickel	Ni 62	1.44	1.47	0.10
Copper	Cu 63	2.59	2.80	0.20
Copper	Cu 65	2.52	2.80	0.20
Zinc	Zn 66	39.9	38.0	2.0
Arsenic	As 75	0.030		
Cadmium	Cd 111	0.223	0.233	0.004
Cadmium	Cd 112	0.229	0.233	0.004
Cadmium	Cd 114	0.230	0.233	0.004
Tin	Sn 118	0.054		
Tin	Sn 120	0.049		
Antimony	Sb 121	0.006		
Antimony	Sb 123	0.005		
Lead	Pb 206	0.152	0.167	0.015
Lead	Pb 207	0.157	0.167	0.015
Lead	Pb 208	0.170	0.167	0.015

F) Results of ICP-MS Analysis (cont.): Results of analysis of two tree cores are shown below. The North Shore Core was collected in a relatively remote location on the northwest end of O`ahu from a tree located downwind from the only road in the area. This location, however, is downwind from the majority of the North Shore of O`ahu therefore receives wind-borne pollution from vehicles traveling in the area as well as from the towns of Waialua and Haleiwa. Additionally, a small general aviation airfield is located upwind of the site.



G) Results of ICP-MS Analysis (cont.): Trace element concentrations in Kiawe from Makua Valley and the North Shore of O`ahu are shown above. Although overall levels are similar, some differences are observed between the two cores. These do not, however, always follow expected trends. For some elements (e.g., Sn, and maybe Cd), concentrations are also higher in the north facing part of the tree, whereas for others (e.g., Co, Ni) no obvious difference is apparent. Cu and Zn appear slightly more enriched in the core from Makua Valley, although Co and Pb are more enriched (and scattered) in the North Shore core. Concentrations of V may be suspect. Potential isobaric interferences from $^{35}Cl^{16}O$, are evidenced by variations in ^{51}V concentrations that appears to be a function on the number of cycles of sample drydown during sample digestion of the Makua Valley Core. Further methods development work is currently underway to address some of these issues.