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Preferred method for removing surface contaminants from geobotanical samples before metals analysis

by

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Abstract

Two sample-cleaning procedures are compared to determine whether trace metal concentrations in leaf tissues are affected by the method of cleaning. Leaves of two deciduous tree species were collected at the end of the growing season for analysis of metal content. Half the leaves were washed with a soap solution and rinsed in deionized water, and half were rinsed without soap-washing. The leaves were then dried, ashed, and analyzed for metal content. For the metals Cu, Zn, and Mn, no significant difference in metal content was found between the washed and rinsed leaves. However, Al and Fe concentrations were generally higher in rinsed leaves than in washed leaves, a fact that may be of significance for acid rain and related studies.

Introduction

Before leaves are analyzed for metal content, residues from soil, rain, dust, and other contaminants must be removed from the leaf surfaces. No standard procedure has been established for safely and thoroughly removing these contaminants without altering metal concentrations within the leaf tissues. Sonneveld and van Dijk (1982) suggest washing with a weak hydrochloric acid or detergent (Teepol) solution. Chapman and Pratt (1961) recommend a weak detergent or Ivory soap solution. Mason (1953) uses a detergent solution in an ultrasonic bath. Some researchers avoid any washing of leaves, whereas others give leaves a quick rinse in the nearest stream.

The purpose of any given study is an important factor in deciding how or whether to clean leaves. We planned to analyze the leaves for metal concentrations. Therefore, we needed to remove surface contaminants, while preserving even small traces of any elements that occurred within the leaf tissues. Because we were collecting large quantities of leaves every day for several weeks and cleaning them each night, our cleaning procedure had to be fast and thorough, but careful so as to avoid damaging the leaves.

To test the effectiveness of rinsing versus soap-washing techniques for removing surface contaminants without removing metals from within the leaf, we collected leaves from canopy trees in North Carolina and subjected half to one treatment and half to the other. We compared results from analyses of metal concentrations to determine whether rinsing alone is adequate.

Methods and Materials

Fresh leaves were collected from canopy trees in early October, 1983, at the end of the growing season, near Asheboro, North Carolina. Red maple (*Acer rubrum*) was collected at six sites and white oak (*Quercus alba*) at five. Leaves were collected from several individuals of each species at each site. All leaves of one species at one site were then mixed together as one sample, to avoid individual variation. The leaves were collected into plastic sample bags and washed or rinsed the same day. Half the leaves were first gently washed in a mild, pure soap solution. The other half were washed the same way, but without soap. All leaves were rinsed once in tap water and then in two changes of deionized water. They were airdried overnight on disposable lab towels and placed in clean plastic bags. A few days later the leaves were unpacked and completely dried in a forced-draft oven for 72 hours. They were then ground in a Waring laboratory blender and stored in glass jars in a closed cabinet.

In January, 1984, the ground leaf samples were ashed in porcelain crucibles at 500°C and digested using nitric and hydrochloric acids following methods developed by T. Harms, U.S. Geological Survey, Denver. The digested samples were analyzed using induction-coupled plasma emission (ICP) by J. Motooka, U.S. Geological Survey, Denver.

Soap-washed and rinsed leaves were compared for copper, zinc, manganese, iron, and aluminum concentrations. Results of the ICP analyses were compared using the Wilcoxon Signed Rank procedure (Gibbons, 1976). This test takes into account both the sign and the magnitude of the difference of each pair of observations. A pair of observations consists of the number of micrograms per gram of ash of one metal in a rinsed sample and in a washed sample. The absolute values of the difference of each pair are ranked, and the ranked numbers of the same sign are added together. The probability of obtaining a particular summed rank value for a given sample size is found in a table in Gibbons (1976). As no particular direction of difference was expected between the two treatments, the hypothesis set was formulated with a two-sided alternative. The null hypothesis (H) assumes that the two treatments do not differ. Because accepting a false null hypothesis is a more serious error in this situation than rejecting a true one, the critical level chosen as a cut-off point for accepting H is $P \leq 0.10$ (10%).

Results and Conclusions

Metal concentrations in rinsed and washed maple and oak leaves are presented in Table 1. Application of the Wilcoxon Signed Rank procedure yielded the probability values in Table 2. Probability values show that the effects of the two treatments do not differ significantly for copper, zinc, and manganese. Iron values show no difference in white oak, but do indicate a potential treatment difference in red maple. With two exceptions (white oak, sites 1 and 5), iron concentrations for both species are lower in soap-washed leaves than in those washed without soap (Table 1). Aluminum concentrations of both species appear to be affected by the method of treatment, with red maple once again showing the clearest difference. In all cases, aluminum values are lower in washed leaves.

Soil aluminum and iron are more available to plants as soil pH decreases (Kramer and Kozlowski, 1979). Therefore, these two elements may be important constituents in acid rain and soil acidity studies. Because both elements seem to be partially removed from leaves by washing with soap, rinsing alone may be the preferred treatment. However, these elements in particular may be occurring in the surface contaminants themselves, in which case soap-washing would be the preferred cleaning method.

For measurement of the heavy metals copper, zinc, and manganese, rinsing is an appropriate treatment. Leaves are most easily and effectively cleaned when fresh, and therefore are cleaned in the field during long collecting trips. Because rinsing is fast, simple, and less likely to damage the leaves or cause loss of metals, it is preferred over soap-washing with rinsing.

Table 1. Concentrations of elements in washed and rinsed leaves of two tree species. Values in micrograms per gram of ash. (R)=rinsed (W)=washed

Site #		1	2	3	4	5	6
				RED MAPLE			
Cu	(R)	303	202	96	182	178	218
	(W)	216	187	98	208	186	192
Zn	(R)	554	326	344	362	413	322
	(W)	512	353	378	386	447	362
Mn	(R)	17789	12274	15922	25766	22108	25064
	(W)	17242	16494	14158	25714	12535	22036
Fe	(R)	1969	395	882	818	441	756
	(W)	766	379	462	548	419	526
Al	(R)	844	347	713	680	641	557
	(W)	169	137	147	302	281	209
				WHITE OAK			
Cu	(R)	68	-	84	44	72	117
	(W)	82	-	72	68	96	141
Zn	(R)	121	-	136	112	100	308
	(W)	136	-	126	116	152	230
Mn	(R)	15074	-	12130	15794	10514	26416
	(W)	11510	-	7014	22860	9345	24217
Fe	(R)	184	-	336	507	354	1061
	(W)	371	-	247	429	388	543
Al	(R)	383	-	363	390	312	1123
	(W)	222	-	164	298	311	618

Table 2. Probability values from Wilcoxon Signed Rank procedure (Gibbons, 1976). Values give probability that treatments do not differ.

Critical Level: $P \leq 0.10$

Metal	Red Maple	White Oak
Copper	.625	.124
Zinc	.438	1.00
Manganese	.312	.624
Iron	.032	.624
Aluminum	.032	.062

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