L. Gough

The Chemistry of Fruits and Vegetables, Yakima River Valley, Washington, and the Influence of the 1980 Mount St. Helens Ash-Fall Episodes

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By L. P. Gough, H. T. Shacklette, J. L. Peard, and C. S. E. Papp

Element concentrations in samples of eight types of produce are reported for collections taken before and after ash deposition, and the importance of compositional differences is assessed

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ABSTRACT

In September 1980, following several months of Mount St. Helens ash-fall episodes, samples of produce (apples, American and European grapes, peaches, pears, plums, potatoes, and tomatoes) were collected from farms in the Yakima River valley, Washington. We compared the chemistry of the samples with that of similar samples that had been obtained 7 years earlier. The concentration of 24 elements, the ash yields, and the soil pH of samples of the two collections were determined. By comparing data from the two collections the influence of environmental sources, including the deposition of Mount St. Helens ash, was evaluated.

Comparisons of post- and pre-ash-fall concentrations of elements in produce yielded differences that are difficult to interpret. Post- to pre-ash-fall mean ratios showed that sodium and potassium (alkali metals); phosphorus and boron (which form complex anions); and aluminum, copper, and manganese (metal cations) commonly occurred at higher concentrations in 1980 than in 1973 (calcium was also higher but only in two produce types) and may reflect the influence of the ash fall. Volcanic-ash leachate studies reported in the literature have shown that, in general, these element groups are easily removed as ionic solutes: their mobility and availability for produce assimilation and tissue incorporation are great. There were, however, no discernible relationships between ash-fall depth and produce chemistry for a given produce type or between the chemical compositions of similar produce types. Results of a variance analysis showed that more of the variability in produce chemistry occurred at a local scale (between replicate samples of the same produce) than occurred between samples of the same type of produce among adjacent fields. This means that, in general, intrinsic element-uptake characteristics of plants are more important to differences in produce chemistry than are localized environmental influences—such as volcanic ash. We conclude that the ash-fall episodes of 1980 had very little direct effect on produce chemistry.

Finally, concentrations of the environmentally important elements (As, B, Cd, Hg, Mo, Ni, Pb, and Se) do not appear unusually high in either the 1973 or 1980 collections.

INTRODUCTION

Between September 7 and 10, 1973, samples of various kinds of fruits and vegetables were collected in the Yakima River valley orchards, vineyards, and farms as part of a nationwide assessment of regional patterns in the element content of fresh produce (Shacklette, 1980). The 1980 eruptions of Mount St. Helens, and particularly the major eruption of May 18, gave us an opportunity to assess the effects of the ash-fall episodes on the element concentration in the same kinds of produce that had been sampled 7 years before. Because of the 7-year interval, however, different analytical procedures were used for some measured parameters than were used in 1973.

Although a number of tephra eruptions by Mount St. Helens occurred in the spring and summer of 1980 (Christiansen and Peterson, 1981), the May 18 episode was by far the most significant event for the Yakima River valley. The amount of ash deposited in the valley from that one event varied (fig. 1), but as much as 10 mm accumulated in a 10-hour period over most of the city of Yakima. Our study sites were variable in the depth of compacted ash observed and in general exceeded the uncompacted depths for the May 18 episode as noted by Sarna-Wojcicki and others (1981). This discrepancy can probably be attributed to errors associated with base-map resolution (we dealt with a comparatively small area) and the area having received some fallout from other volcanic eruption episodes.

To minimize the influence of additional, perhaps equally important, environmental factors (other than the ash fall) on the chemistry of the produce during the 4 months following the major eruption, we sampled the same material in the same manner as that of the previous study, at the same time of year (mid-September), and usually at the same farms and fields. Also, in order to control any influence that produce type might have on the element content, the same fruit or vegetable (and in some instances, the same cultivar) was sampled. Despite these precautions, other environmental factors, such as the quality and quantity of fertilizer and pesticide applications, could change the chemistry of the substrate (and thus potentially the chemistry of produce) over the long term.

Many of the results from early studies on the physical, chemical, biological, and sociological consequences of the 1980 Mount St. Helens volcanic episodes are documented in U.S. Geological Survey Professional

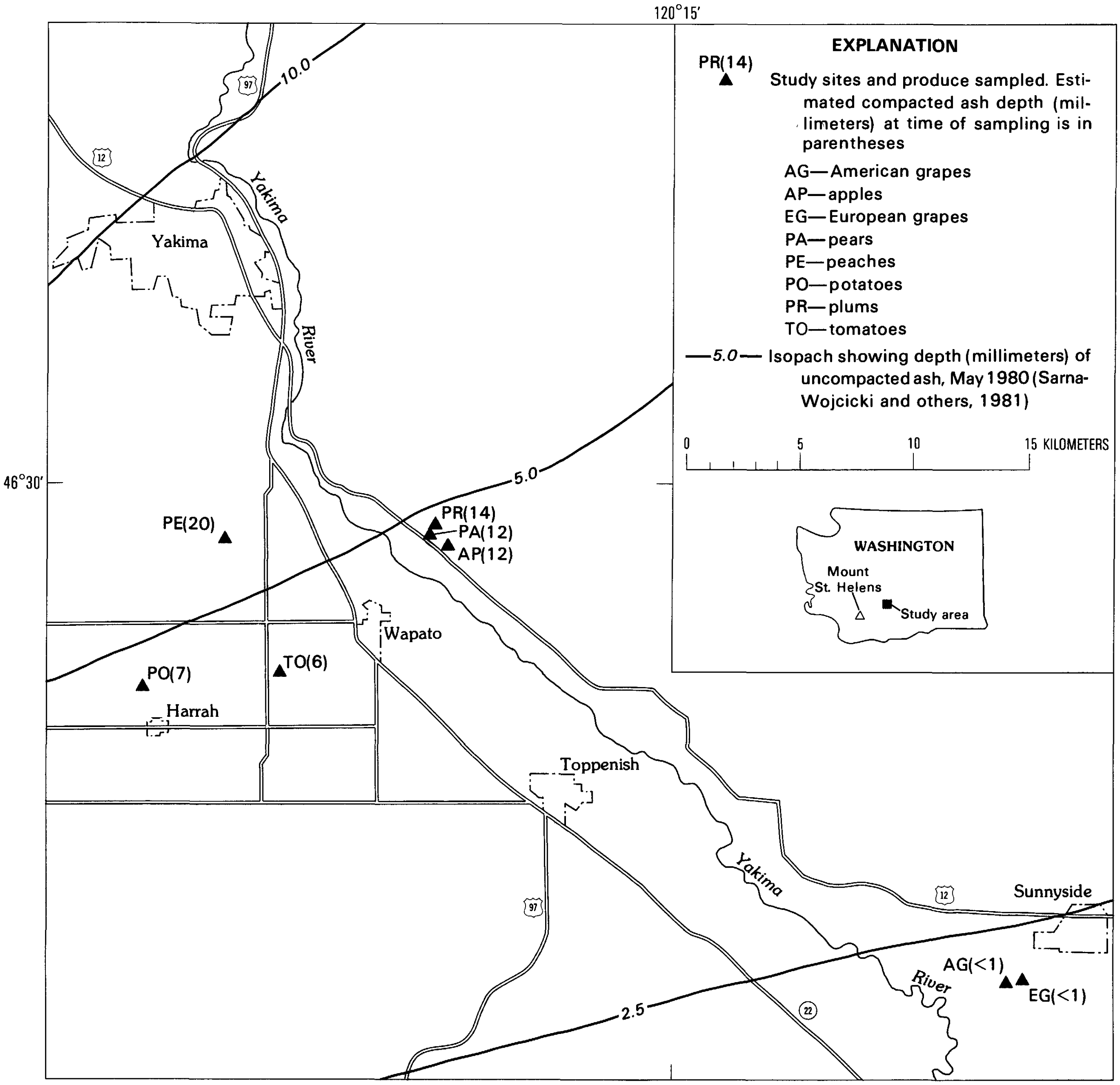


Figure 1. Map of the study area showing the location of sampling sites, types of produce sampled, and approximate volcanic ash depths.

Paper 1250 (Lipman and Mullineaux, 1981). Studies that deal specifically with the effect of the tephra deposits on agricultural soils include U.S. Department of Agriculture (1980), Washington State University (1980), Goldin (1982), and Sneva and others (1982). Gough and others (1981) examined the effect of the May 18, 1980, ash fall on the chemistry of soft, white winter wheat and supporting soils along a north-south transect, near Ritzville, Wash. Their study sites varied in the depth of ash received from less than 0.1 to 40 mm. Results from that study showed that ash depth had little effect on the exchange status of the soil but did have an inverse effect on soil pH and a direct effect on wheat sulfur levels. In an unpublished follow-up study, one year after the eruption, we found that the soil trends noted in 1980 were ameliorated and that background levels of trace metals had been achieved, indicating a return to equilibrium. Levels of sulfur and several other elements, however, were found to be slightly elevated in wheat from areas that received greater than about 20 mm of ash.

Whereas the main emphasis of this study was to compare the chemistry of Yakima River valley produce before and after the eruptions of Mount St. Helens, the element contents reported here were also compared to those from the literature in order to identify unusual values. The reviews of produce chemistry by Beeson (1941) and Chapman (1966) were particularly useful. Eight additional papers were also examined (Diem, 1962; Warren and Delavault, 1971; Warren and others, 1971; Hutchinson and others, 1974; Ward, 1977; Whiting and others, 1978; Auermann and others, 1979; and Tabekhia, 1980). Our literature comparison revealed no unusual concentration values in this study; however, a large amount of variability exists between studies due to differences in plant varieties, areas of production, cultivation practices, and methods of collection and analysis.

ACKNOWLEDGMENTS

We thank Donald A. Chaplin and Brooke Peterson, County Extension Agents, Yakima County, for information concerning the effects of the ash fall on the local crop yield and quality, and the methods used by farmers to ameliorate the detrimental physical effects of the ash fall on orchards, vineyards, and fields. The chemical data on the element content of the fruits and vegetables were provided by coauthor C. S. E. Papp and by M. J. Malcolm, T. F. Harms, and A. Mast. We also wish to thank the following individuals or farms in the Yakima River valley for giving us permission to sample and for providing information concerning their particular crop(s): Don McDonald (pears and plums), Howard Olson (apples), Matsumara Farms (tomatoes), Garret Schilperoord (potatoes), Albert Neuhaus (grapes), and Pride Packing Co. (peaches).

METHODS

Sampling Design and Statistical Methodology

The natural-variation and analytical-error components of the total variability in the chemical data for this study were measured using a one-way, four-level, nested, analysis-of-variance (AoV) design similar to those described in detail by Miesch (1976). The total variability was partitioned, for each individual produce type, among four fields, between two sites within each field, between two samples within a site, and between duplicate analyses of the same sample. The purpose of such a design was to measure the variance components for each produce type so that the possible influence of the addition of volcanic ash to the soil could be better defined. (See the discussion in the "Variance Analysis" section.)

The design was unbalanced below the "between sites within fields" level, which allowed us to economize both in field time and in the number of samples analyzed without significantly affecting the variance estimates at each level.

Twelve samples of each produce type were collected. Concentrations of some elements occurred below the lower limit of determination (LLD) for the particular analytical method used (table 1). Table 2 lists the number of values recorded above the LLD, by produce type, for each element in both the pre- and post-ash-fall studies.

Statistical treatment of data was not performed if the number of values below the LLD for a given produce type exceeded four (one-third of the total, table 2). If, however, one to four of the values were below the LLD, then the mean was calculated using the technique of Cohen (1959). The analysis-of-variance procedure cannot use values below the LLD, and substituted values equal to 0.7 times the LLD were used when, as above, censoring did not exceed one-third. In order to better approximate normal frequency distributions the data were first transformed to natural logarithms.

Sample Collection and Preparation

Fruits and vegetables.—At each orchard, vineyard, or farm (fig. 1), a large area usually encompassing several hectares was selected for sampling. The maturity of the produce, the accessibility of the area, the proximity of the area to the 1973 collections (the same fields when possible), and the wishes of the farmer were considered in the selection process. Once an area was chosen it was visually divided into four equal units that were designated as "fields." Two sampling "sites" were then selected at random within each field. Depending on the type of produce sampled, a site was variously defined as a single tree, a vine, a clump, or a row. Therefore, duplicate samples at a site meant that (1) apples, plums, pears, peaches, and grapes were collected on opposite sides of the same tree or vine; (2) tomatoes were collected from adjacent plants within a row; and (3) potatoes (those remaining in the field after a recent harvest) were collected from the same general area within a row. The material for duplicate analyses of a single sample (level four of the AoV) was selected at random from the samples of the sites-within-fields level and constituted one-third of all samples. The actual splitting of the samples was not made until the material had been dried and ground in the laboratory.

In the field, the fresh produce was placed in polyethylene bags, sealed, and chilled to retard spoilage. Later the same day the material was prepared as if it were to be eaten directly or cooked (without actually being cooked). The type of produce, its scientific name,

Table 1. Analytical methodologies and estimated lower limits of determination (LLD) for the pre- and post-ash-fall (1973 and 1980, respectively) Yakima produce chemistry studies

[Values are in parts per million; leaders (---) mean no data; AAS, atomic absorption spectrophotometry (Harms, 1976); FL-AAS, flameless atomic absorption spectrophotometry (McHugh and Turner, 1975); ES, D-C arc emission spectroscopy (Dorrzapf, 1973, as modified by Neiman, 1976); ICP, inductively-coupled plasma emission spectroscopy (Lichte, 1982); FLUR, fluorimetry (Harms and Ward, 1975; Huffman and Riley, 1970); SIE, selective ion electrode (Ficklin, 1970); COLR, colorimetry (Harms, 1976); TURB, turbidimetry (Tabatabia and Bremner, 1970)]

Element	1973 study		1980 study	
	Analytical method	Estimated LLD	Analytical method	Estimated LLD
	Dry material of sample			
As...........	AAS	0.05	AAS	0.05
F	---	---	SIE	1
Hg...........	FL-AAS	.01	FL-AAS	.01
Se...........	FLUR	.005	FLUR	.003
S, total.....	TURB	100	TURB	100
	Ash of sample			
Al...........	ES	150	ICP	300
B	ES	50	ICP	20
Ba...........	ES	3	ICP	5
Ca...........	AAS	100	AAS	100
Cd...........	AAS	.2	AAS	1
Co...........	AAS	1	AAS	1
Cr...........	ES	1.5	ICP	1.5
Cu...........	ES	1	ICP	5
Fe...........	ES	10	ICP	300
K	AAS	100	AAS	100
Mg...........	ES	20	AAS	20
Mn...........	ES	1	ICP	20
Mo...........	ES	7	ICP	10
Na...........	AAS	25	AAS	25
Ni...........	ES	10	ICP	10
P	COLR	100	COLR	100
Pb...........	ES	20	ICP	20
Sr...........	ES	10	ICP	10
Zn...........	AAS	10	ICP	10
Zr...........	ES	20	ICP	10

cultivar name (cv.), and method of preparation follow: American grape (*Vitis labruscana* Bailey, cv. Concord) and European grape (*Vitis vinifera* L., cvs. Black Manukka and Thompson Seedless)—bunches washed and drained, berries removed from stems; apple (*Pyrus malus* L., cv. Red Delicious), peach (*Prunus persica* Batsch., cv. Gold Medal), pear (*Pyrus communis* L., cvs. Bosc and Bartlett), and plum (*Prunus domestics* L., cv. Italian)—fruit washed and drained, peeled, core or seed (pit) removed, sliced; potato (*Solanum tuberosum* L., cv. unknown, russet and red types)—tubers washed, drained, peeled, sliced; tomato (*Lycopersicum esculentum* Mill., cv. unknown)—fruits washed, drained, sliced. Where there were two cultivars collected for a given kind of produce (European grapes, pears, and potatoes), half of the samples were of one cultivar and half were of the other. For discussion purposes, however, they are combined.

Following their preparation the samples were sealed in double-thick polyethylene bags, chilled, boxed, and shipped to the Denver laboratories of the U.S. Geological Survey where they were immediately frozen. In the laboratory, the bags were opened wide and placed in shallow aluminum pans; the material in the bags was then dried in a forced-air oven at a temperature of 38–40°C. After several days the samples that appeared dry were removed from the oven and weighed. They were then returned to the oven where

Table 2. Number of samples with concentrations above the lower limit of determination for each of the eight kinds of produce collected in the pre- and post-ash-fall (1973 and 1980, respectively) Yakima produce chemistry studies

[Leaders (--) mean no data; a total of 10 samples per produce type was collected in 1973 and 12 in 1980]

Element	Apples		American grapes		European grapes		Peaches		Pears		Plums		Potatoes		Tomatoes	
	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980
Al.......	10	12	10	12	10	12	10	11	8	9	8	12	7	12	5	12
As.......	[1]7	1	[1]4	1	[1]0	2	2	9	3	0	[2]0	0	0	0	[2]1	0
B	10	12	10	12	10	12	10	12	10	12	10	12	8	12	10	12
Ba.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Ca.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Cd.......	5	6	6	0	5	3	6	0	7	2	3	4	10	7	10	10
Co.......	2	8	0	4	0	7	5	5	7	11	1	10	10	10	5	12
Cr.......	1	9	4	3	2	4	9	5	4	8	2	7	1	4	3	4
Cu.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
F	--	12	--	12	--	12	--	12	--	12	--	12	--	12	--	12
Fe.......	10	10	10	11	10	9	10	5	10	6	10	4	10	10	10	8
Hg.......	1	1	2	4	0	2	1	0	2	3	0	0	0	0	1	0
K	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Mg.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Mn.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Mo.......	2	0	1	0	0	0	0	0	0	2	0	1	5	4	2	1
Na.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Ni.......	0	10	1	5	0	2	7	10	4	9	1	8	9	7	9	10
P	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Pb.......	0	3	1	2	0	0	1	1	0	2	1	0	0	2	0	0
S	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Se.......	10	6	10	10	7	8	6	0	7	1	5	6	10	5	10	12
Sr.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Zn.......	10	12	10	12	10	12	10	12	10	12	10	12	10	12	10	12
Zr.......	0	2	0	1	3	12	0	1	1	5	1	3	0	1	0	1

[1]Because of an insufficient amount of material in one sample, the total was nine samples.
[2]Because of an insufficient amount of material in two samples, the total was eight samples.

they remained 1 day and were then weighed again. This process was continued until no further loss in weight occurred (±0.1 g). Starchy samples (for example, potatoes) dried to a constant weight in 3–5 days, whereas samples with a high sugar content (peaches and grapes), or with a high water content (tomatoes), required as much as 2 weeks of drying to attain a constant weight. The dried samples were pulverized or shredded in a stainless-steel blender.

Soils.—At each location where a produce sample was collected a soil sample was also taken. In order to decrease the tendency of the volcanic ash to be moved around by winds, farmers in the Yakima River valley commonly disked their fields and orchards soon after the ash fall. This served to incorporate most of the ash into the upper 15–20 cm of the soil. Our samples, therefore, were a composite of the material from the surface down to about 20 cm. At a few study sites, such as the peach orchard, the substrate had not been disked. We composited the surface ash layer with the soil at these locations.

All samples were placed in manila envelopes and allowed to dry at ambient temperatures. In the laboratory the samples were homogenized and a slurry of equal parts soil and water (by weight) was prepared for pH determinations (Peech, 1965).

Analytical Methodology

The produce samples were ashed at 500°C in a muffle furnace for about 14 hours, and aliquots were made for those analytical procedures requiring ash (table 1). Ashing success varied greatly among produce types. For example, peaches and plums (which, after drying, formed a semisoft sticky mass) required three 24-hour ashing cycles before the ash became light gray in color. Tomatoes, although not as high in sugar as peaches and plums, also required three ashing cycles. Grapes, apples, potatoes, and pears ashed completely after only one cycle. The error introduced into the data by the problems associated with incomplete ashing is included in the measurement of variability in analytical precision (level four of the AoV design). However, the effect of this error on the accuracy of our data cannot be separated from effects of the other error factors, although incomplete ashing is known to reduce the calculated element concentration values.

We report analytical data for the concentration of 25 elements in fruits and vegetables. All except fluorine, which was not reported in the earlier study, can be compared to the 1973 data. Comparisons of analytical data generated over time can be difficult because of alterations that occur in methodologies and in sample-preparation procedures. In general, about half of the element concentrations determined 7 years ago used the same methods as those used in this study (table 1). However, in 1973 concentrations of Al, B, Ba, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, and Zr were determined semiquantitatively by DC-arc emission spectroscopy. Shallow electrodes filled with a mixture of plant ash, quartz, sodium carbonate, and graphite were burned; the spectra were recorded on photographic plates and then visually read. The relative standard deviation for this method is ± 70 percent. In 1980, concentrations of these elements (except magnesium) were more precisely determined by inductively coupled plasma emission spectroscopy. This procedure utilized ashed plant material that had been totally dissolved by a multi-acid bomb digestion. The determinations of magnesium in 1980 were also performed on solutions of plant ash but by atomic absorption spectrophotometry. Although both studies utilized internal reference standards that allow the analysts to check their data with figures generated over time and with different plant materials, the influence of unknown analytical biases is possible. The ability of the analytical method to detect low concentrations of elements and the changes that have occurred with time in the detection capabilities of the analytical methods are given in table 1.

RESULTS AND DISCUSSION

Element Mean and Ratio Comparisons

Table 3 lists geometric means of the concentration of 24 elements in the 10 samples of each produce type that were collected in 1973, and the means of 12 samples of the same produce types that were collected in this study. A test of significance between the means of the two studies was not performed because of (1) difficulties associated with the interpretation of independence among samples collected in a hierarchical AoV design, and (2) differences in analytical methods between the studies for 13 of the elements (see "Analytical Methods" section) having undoubtedly introduced some undefinable analytical bias. Subjective assessments of the magnitude of the differences among the means for each produce type can be made, however, by comparing the relative magnitude of the differences. In general, means separated by a factor of three or more are unusual.

Although the means presented in table 3 are important in evaluating the level of the occurrence of an element of interest in produce, these data, presented in this manner, are difficult to interpret with reference to the ash-fall event. To better display the relative magnitude of the differences between the means, the post- to pre-ash-fall or pre- to post-ash-fall ratio of the means was calculated. Figure 2 is a bar graph of these ratios in which a one-to-one relation is depicted as the center line. Bars above the line show relations of post-ash-fall means that are larger than the pre-ash-fall means and, conversely, bars below the line depict ratios with larger pre-ash-fall means. The elements presented either had especially large mean differences (table 3) or were found by other workers to be components of Mount St. Helens ash.

Availability of Ash Solutes

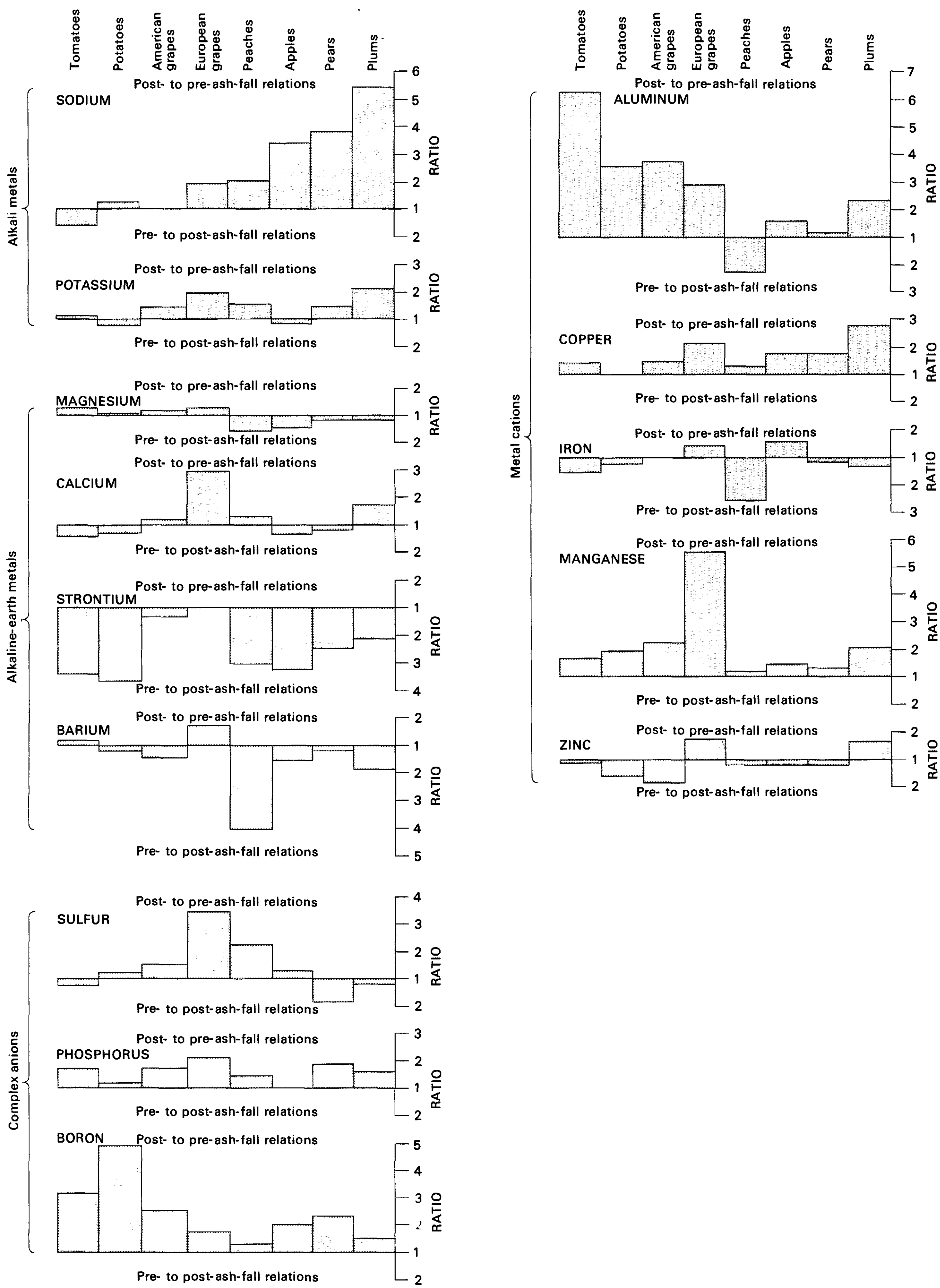
To demonstrate an ash-fall effect on the element content of produce, we expected to observe large post-to pre-ash-fall ratios. Further, those elements in the ash that were found to be highly mobile should be the ones most available for absorption by the plants. Studies by Taylor and Lichte (1980) and Fruchter and others (1980) demonstrated that the mineralogy and elemental composition of the ash differed with increasing distance from the volcano. These authors also showed that certain of the heavy metals were found as solutes in water leachates but at concentrations that were of no environmental concern. Hinkley and Smith (in press) found that a deionized water leach of fresh ash (ash that had not been exposed to rain) removed as much as 0.5 percent of the total amount of certain alkali and alkaline-earth metals and about 45 percent of the total amount of sulfate sulfur. Further, they found that the neutral water leach removed about 2–6 percent of the total content of nickel, cobalt, manganese, and calcium. In an additional treatment using an acid leach, they found that significantly larger amounts of most elements were released when compared to the amounts in the water leach. The acid treatment was found to remove elements from the primary igneous minerals in the ash, whereas the water leach removed readily soluble surficial element deposits. They concluded that most of the solutes were probably removed as a single "pulse" during the first rain following ash deposition. The cities of Yakima and Sunnyside (located at each end of the Yakima River valley study area, fig. 1) received their first substantial rainfall, 11 mm and 21 mm, respectively, 8 days after the May 18 ash-fall episode (U.S.

Table 3. Geometric means of 24 elements (plus ash yield and soil pH) in the ash of eight kinds of produce collected before (1973) and after the major Mount St. Helens eruption of May 18, 1980

[1973 and 1980 means are based on 10 and 12 samples, respectively; leaders (--) indicate that the mean was not calculated because of an excessive number of values below the lower limit of analytical determination; concentrations of As, Hg, and Se are on a dry weight basis]

Element, ash, or	Apples		American grapes		European grapes		Peaches		Pears		Plums		Potatoes		Tomatoes	
soil pH	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980	1973	1980
Ash, pct...	1.7	1.7	4.7	4.0	3.1	3.8	8.9	5.6	1.9	4.0	4.3	6.7	4.0	3.4	11	9.0
Al, ppm[1]...	490	720	500	1700	460	1200	1200	570	320	360	290	620	190	600	130	710
As, ppm....	.070	<.05	.029	<.05	<.05	.05	<.05	.07	<.05	--	<.05	--	<.05	<.05	<.05	--
B, ppm[1]...	450	790	270	640	310	490	560	630	580	1200	610	860	58	250	81	220
Ba, ppm[1]...	91	59	91	70	36	59	55	20	120	110	60	36	29	27	13	14
Ca, pct....	1.1	.90	2.9	3.2	1.0	2.6	.49	.59	1.4	1.3	.62	.99	.67	.56	1.0	.78
Cd, ppm....	.15	1.2	.17	--	.13	.49	.18	--	.22	<1.0	.11	.61	2.8	1.3	2.2	2.2
Co, ppm....	.46	1.2	<1	1.2	.69	.84	1.0	2.0	<1	1.9	3.6	2.4	.74	2.6	.74	2.6
Cr, ppm[1]...	<1.5	9.2	.28	<5.0	<1.5	3.7	3.2	4.6	.95	6.8	<1.5	5.8	4.5	3.7	.91	3.8
Cu, ppm[1]...	61	97	61	86	43	85	70	87	110	180	33	83	98	97	73	98
Fe, ppm[1]...	350	520	650	680	360	500	750	320	300	300	270	220	520	490	550	380
Hg, ppm....	<.01	<.01	<.01	<.01	<.01	<.01	<.01	--	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
K, pct....	36	32	21	27	14	25	20	30	21	30	16	30	42	38	34	37
Mg, pct[1]...	1.6	1.2	1.5	1.7	1.1	1.3	1.5	1.1	1.5	1.4	1.2	1.1	2.1	2.3	1.6	1.9
Mn, ppm[1]...	56	74	48	100	24	120	78	83	79	94	45	81	94	170	110	170
Mo, ppm[1]...	4.3	<10	<7	--	<7	--	--	--	--	<10	<7	<10	5.7	<10	<10	<7
Na, ppm....	590	1700	1200	1200	530	900	190	340	420	1400	120	560	1400	1600	3600	2200
Ni, ppm[1]...	<10	26	<10	9.7	<10	17	15	24	7.4	21	<10	13	16	10	15	19
P, pct....	2.2	2.2	1.3	2.1	1.4	2.7	2.4	3.3	1.5	2.6	1.3	2.0	4.6	4.9	2.5	4.3
Pb, ppm[1]...	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
S, ppm.....	180	190	490	650	230	690	290	540	690	400	290	270	1200	1300	2100	1900
Se, ppm....	.0023	.0040	.018	.004	.0051	.003	.0044	<.003	.007	.003	.0036	<.003	.008	.003	.035	.011
Sr, ppm[1]...	130	44	240	170	130	130	82	29	150	66	120	63	100	29	92	29
Zn, ppm....	49	46	98	57	50	78	120	110	120	110	100	160	380	260	250	270
Zr, ppm[1]...	<20	14	<20	<10	<20	<10	<20	<10	<20	8.6	<20	<10	<20	<10	<20	<10
pH.......	6.6	6.3	7.4	7.6	7.9	7.6	5.7	6.6	6.3	6.2	6.8	7.2	7.1	6.7	6.6	5.8

[1]Possible undefinable analytical bias present because of the use of different methodologies (see "Analytical Methodology" and "Element Mean and Ratio Comparisons" sections).


Tomatoes
Potatoes
American grapes
European grapes
Peaches
Apples
Pears
Plums
Alkali metals
SODIUM
POTASSIUM
Alkaline-earth metals
MAGNESIUM
CALCIUM
STRONTIUM
BARIUM
Complex anions
SULFUR
PHOSPHORUS
BORON
Metal cations
ALUMINUM
COPPER
IRON
MANGANESE
ZINC
Post- to pre-ash-fall relations
Pre- to post-ash-fall relations
RATIO

Department of Commerce, 1980a,b). Within 1 month of the ash fall, these two recording stations had received a total of 31 mm and 42 mm of rainfall, respectively.

Ash Solutes and Produce Chemistry

We conclude from the ash and leachate composition studies just mentioned that numerous cations and anions were probably available for either foliar or root absorption or both as a result of the precipitation events of the first month. Only a very small probability exists that these ions were absorbed directly by the edible portion of the produce because the peaches, apples, pears, plums, and grapes were immature at the time of ash fall (the trees having recently set fruit) and the tomatoes and potatoes had only just been planted. Figure 2 gives the post- to pre-ash-fall ratios for selected elements found by Hinkley and Smith (in press) to be important constituents of both the water and acid leachates. The produce is ordered from left to right based upon the ratios (low to high) calculated for sodium. Sodium was chosen as the base against which the other elements are compared because (1) the ratios showed large variability, (2) Hinkley and Smith found it to be one of the major water- and acid-soluble constituents of the ash, and (3) it is essentially not added to fields or orchards through irrigation waters or other sources.

Several conclusions are possible from examination of figure 2:

1. The alkali metals, sodium and potassium, are more highly concentrated in most types of produce grown after the ash fall. Plums showed the greatest difference between post- and pre-ash-fall levels for both elements (sodium, about a fivefold difference; potassium, about a twofold difference; table 3). This increase could have resulted from an ash-fall effect, although fertilization practices may have been the source of the additional potassium. Commonly, however, neither phosphorus nor potassium is added to Yakima River valley orchard crops.

2. In the majority of produce the alkaline-earth metals (magnesium, calcium, strontium, and barium) were more highly concentrated in the pre-ash-fall samples; exceptions were calcium and barium in European grapes and calcium in plums. This trend means either no demonstrable ash-fall effect for these elements or a negative effect. For example, calcium and strontium have generally opposite trends and could represent competitive exclusion; that is, because these elements are physiologically similar, an increase in available calcium could depress the incorporation of strontium—the reverse situation could also occur.

3. The anions SO_4^{2-} and PO_4^{3-} were found by Hinkley and Smith (in press), using the acid leach, to be readily removed from the ash. Figure 2 shows that levels of phosphorous in produce were generally higher (levels of sulfur only occasionally higher) following the ash fall than before. Changes in the levels of phosphorous and sulfur are not the result of fertilization practices because, except for tomatoes and potatoes, neither is added to orchards or vineyards on a routine basis in the Yakima River valley. Also, Gough and others (1981) found sulfur levels in soft, white winter wheat to be positively associated with ash-fall depth and negatively associated with soil pH along an 80-km north-south traverse in eastern Washington State. Boron, another complex anion, was generally found in much greater concentrations in post-ash-fall produce (tomatoes and potatoes showed a threefold and fivefold difference, respectively). Fruchter and others (1980) interpreted boron in Mount St. Helens ash as being in a relatively immobile form. The data of Hinkley and Smith (in press), although somewhat inconclusive, tend to support this generalization. Brooke Peterson (Extension Agent, Yakima, oral commun., 1983) stated that boron is commonly applied to orchard crops as a foliar spray but normally in late fall or early spring. We are uncertain, therefore, as to the cause of the increased boron concentrations in the post-ash-fall samples.

4. Of the transition metals, manganese and copper showed large post- to pre-ash-fall ratios for much of the produce, whereas iron and zinc generally did not. Although the addition of copper could be related to the application of certain fungicides (copper sulfate-based mixtures) to, for example, the stone fruits, a rather uniform post- to pre-ash-fall trend occurs regardless of produce type or fungicide-application history. Both zinc and iron are commonly applied in chelated forms as foliar sprays to combat deficiency problems in orchards. Neither of these elements showed much change between the two studies. Aluminum, another metal cation, was much higher in concentration in the post-ash-fall samples for most produce types.

Soil pH

Table 3 shows very little difference between the soil pH measurements of the two studies. Because the post-ash-fall samples were collected nearly 4 months after the major ash-deposition episode, we do not know what short-term effect, if any, the ash may have had on soil pH—certainly the long-term effect was negligible. Immediately after the ash fall there were numerous

Figure 2 (facing page). Ratios of post- to pre-ash-fall or pre- to post-ash-fall element concentration means for eight produce types; center line depicts a one-to-one relation. The produce sequence is based on the ranking of sodium ratios from lowest to highest.

reports that the tephra was highly corrosive. Hinkley and Smith (in press) postulated that a coating of sulfuric acid on the ash was responsible for this observation. They contended, however, that the acid would have either evaporated or reacted with the available base cations within 1 or 2 hours of ash deposition. Whether or not substrate pH was lowered for longer periods by the net addition of protons from the ionic species that were solubilized is not known. In an area of eastern Washington State that received considerably more ash than did the Yakima River valley, fairly strong inverse relations between ash depth and soil pH were found one month after the ash fall (Gough and others, 1981). If we assume that a temporary decrease in substrate pH occurred during the ash-fall event on May 18, then, in addition to the metal cations that were readily solubilized from the ash, metals in the soil may have been mobilized as well. This combined effect may be responsible for the higher post-ash-fall levels of aluminum, copper, and manganese mentioned in the previous section.

Produce Ratio Patterns and Ash Depth

Only a few ratio patterns appear to be consistent for a majority of the elements tested (fig. 2). In general, post-ash-fall European grapes and pre-ash-fall peaches contained much larger concentrations of most elements than did their pre- or post-ash-fall counterparts, respectively. The pattern for European grapes does suggest an ash-fall effect. Unfortunately, this pattern is not correlated with ash depth. Figure 1 shows that the grapes were actually collected in a field with <1 mm of compacted ash—the least amount of ash encountered for any of the produce study sites. Conversely peaches were collected in an orchard that had 20 mm of compacted ash.

VARIANCE ANALYSIS

Many sources of error in the chemical data could confuse the meaningful interpretation of differences in the element content of produce before and after the ash fall. This error (or variance) can be basically divided into two kinds: natural and analytical. The natural error arises from differences in (1) the external environment of the plant during its development—including fertilization practices, changes in soil geochemistry, water availability, and the presence of volcanic ash in the soil or on the aerial plant parts—and (2) the genetic makeup of the plant which results in the passive absorption, active exclusion, or even large accumulation of elements. The sources of analytical error are inhomogeneity of the sample, the analytical machine-oriented drift with time, and the bias introduced by both the collector and the chemist. If a small proportion of the variance in the data for a given element is analytical and a large proportion is natural, then regional environmentally controlled factors are easier to interpret. Further, if it can be shown that a large proportion of the natural variability in produce chemistry occurs on a regional scale (between fields), so that a very small proportion of the variability occurs locally (between, for example, rows or clumps), then the possible impact of the addition of volcanic ash is more easily demonstrated: a regional ash-fall influence should overwhelm the variability in plant chemistry caused by microhabitat differences between adjacent plants.

Table 4 gives the relative magnitudes of the variance components at each of the four AoV levels for samples of the eight produce types collected in 1980. Because each individual produce type showed generally similar distributions of variance among the four AoV levels, an average of the percent total variance for an element, in a particular level, was calculated across all produce types. These averages were then grouped into 20-percent classes.

The absence of an important regional (among fields) variance component is an argument for the general lack of a strong environmental influence, such as a volcanic-ash affect. Conversely, the large amount of variance at the local level (between sites within a field and between samples within a site) indicates that differences between the element content of individual plants of the same species, or even between samples taken from the same plant, are larger than any environmental differences that are present on a regional scale. Further, the last column in table 4 indicates that a substantial proportion of the total variability in the data in the 1980 collection occurred between duplicate analyses of the same sample. Because, in general, the spread in the data between the highest and lowest value was small, the variability introduced by analytical methodology is larger and would appear more important than the variability caused by natural processes.

SUMMARY AND CONCLUSIONS

1. Concentrations of 24 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, Zn, and Zr) in eight produce types (apples, American and European grapes, peaches, pears, plums, potatoes, and tomatoes) were compared in samples collected before (1973) and after the major tephra-producing eruptions of Mount St. Helens in the spring and summer of 1980. The study sites in this report (orchards, vineyards, and farms) were south and east of the city of Yakima in a rich irrigated agricultural valley that received approximately 0.1–1.0 g/cm^2 of volcanic ash from the May 18 eruption (Sarna-Wojcicki and others, 1981). The volcano is located about 135 km

Table 4. Relative importance of each of four levels in the AoV study design for samples of eight produce types collected in 1980

[Symbols represent classes of the average of the percent total variance for an element in a particular level, across all produce types: * = 1–20 percent, ** = 21–40 percent, *** = 41–60 percent, **** = greater than 60 percent; As, Cd, Hg, Mo, Pb, Se, and Zr are not listed because of an excessive number of values below the lower limit of determination (table 2)]

Element or ash yield	Among fields	Between sites within a field	Between samples within a site	Between duplicate analyses
Ash	*	*	**	**
Al	*	*	***	**
B	*	*	**	**
Ba	*	**	**	**
Ca	*	**	**	**
Co	*	*	**	***
Cr	*	*	*	****
Cu	*	**	**	***
F	*	*	**	***
Fe	*	**	*	***
K	*	*	**	***
Mg	*	**	**	**
Mn	*	**	**	**
Na	*	**	*	***
Ni	*	**	**	**
P	*	**	**	**
S[1]	*	**	***	*
Sr	*	**	*	**
Zn	*	**	*	***

[1]Total sulfur.

to the west-southwest of Yakima; because the ash plume initially traveled in a northerly direction, however, the study area was actually on the southern edge of the tract of major ash deposition. At the time of the September post-ash-fall sampling, compacted ash depths varied from a high of 20 mm (about 8 km south of Yakima) to a low of <1 mm (about 45 km southeast of Yakima).

2. Differences between the element means of the post- and pre-ash-fall collections are difficult to interpret. Ratios of the means of the two collections were calculated and plotted in order to better categorize the differences. The alkali metals (sodium and potassium), the complex anions (phosphorus and boron), and certain of the metal cations (aluminum, copper, and manganese) had many large post- to pre-ash-fall ratios (from >1 to >5) that were characteristic of nearly all of the produce types. The alkaline-earth metals were characterized in general by larger pre- to post-ash-fall ratios. Studies in the literature showed that the trends for the above groups of cations and anions (except the alkaline-earth metals) could be correlated with the ionic solute composition of water and acid leachates of ash. This correlation suggests that produce chemistry may have been affected by the chemistry of the ash fall, assuming that those ions readily leached from the ash were also readily available for plant uptake and incorporation into tissues. On the other hand, ash leachate studies also showed that a reasonably large proportion of the total amount of the alkaline-earth metals was also solubilized; the produce, however, did not reflect this. Further, there were no discernible patterns between ash-fall depth and produce chemistry or between the chemistries of similar produce types (produce in the same plant family). We feel confident that surficial contamination was not the source of the differences noted in produce chemistry because all samples were washed and many (potatoes, pears, peaches, and apples) were also peeled before analysis. The importance of the addition of elements to the soils in the form of fertilizers, or through the application of pesticides, and the impact that these additions might have on changes in produce chemistry are unknown. Conversations with county extension agents and farmers, however, would indicate that, except for the relatively recent recognition that boron applications can increase yields of some crops, fertilization practices have not changed appreciably in seven years.

3. We conclude that any ash-fall effect on the

chemistry of produce in the Yakima River valley was subtle and probably produce-specific. For example, sulfur was found by other investigators to be a common constituent of ash leachates. Sulfur is also easily mobilized and translocated in plant tissue. If sulfur was being contributed by the volcanic ash, only European grapes and peaches (and perhaps American grapes) reflected this contribution.

4. The results of a study design that measured the distribution of the element-concentration variability among samples collected at various distances showed that no major regionally related environmental influence (such as an ash-fall episode) could be defined. In fact, the spread in the data was often quite small, and variability associated with analytical methodology could overwhelm any variability caused by natural events.

5. The levels of all of the environmentally important elements (including As, B, Cd, Hg, Mo, Ni, Pb, and Se) were found to be well within the range considered to be normal for plant tissue in general (Gough and others, 1979).

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