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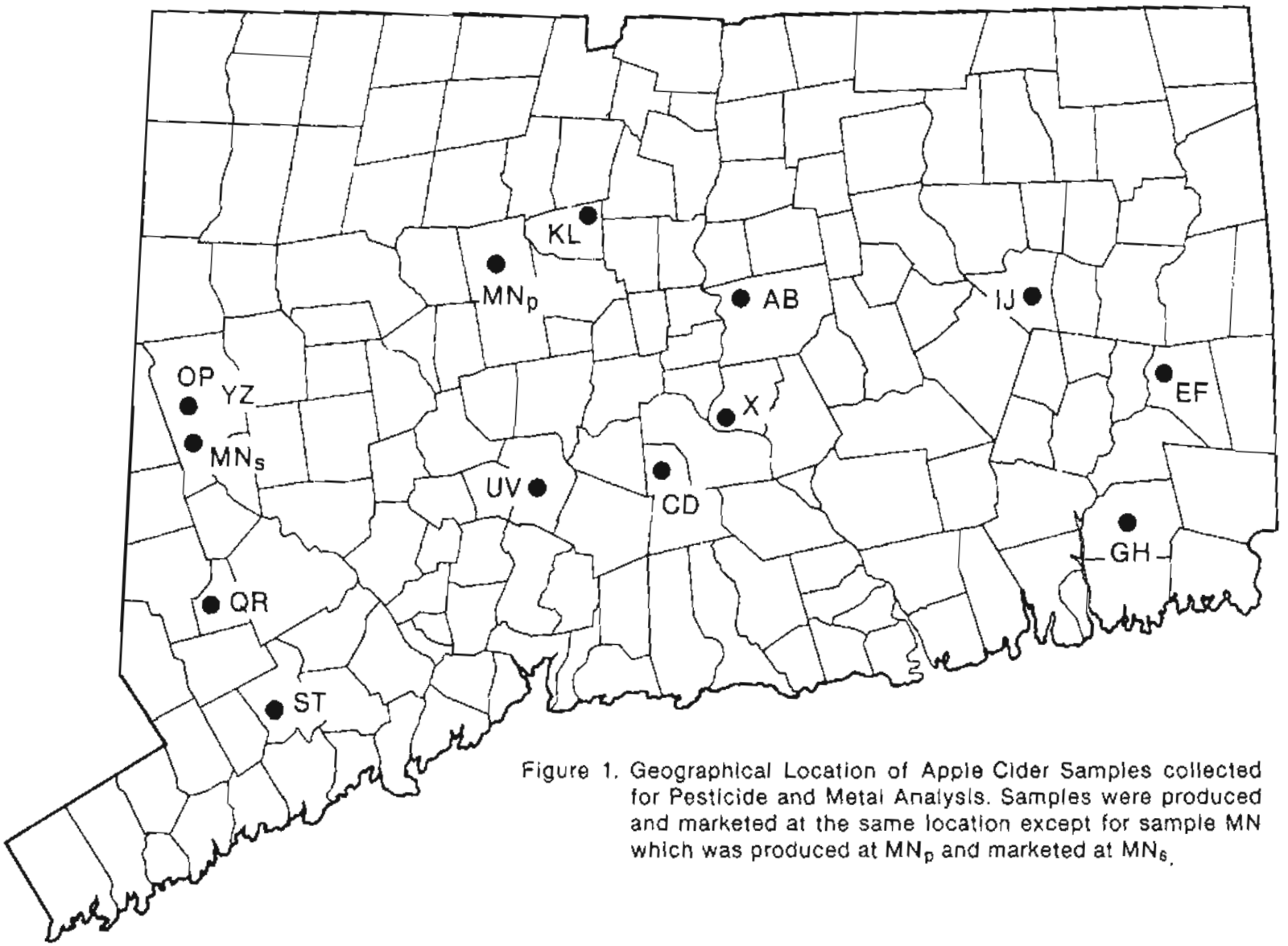

Figure 1. Geographical Location of Apple Cider Samples collected for Pesticide and Metal Analysis. Samples were produced and marketed at the same location except for sample MN which was produced at MN_p and marketed at MN_s.

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INTRODUCTION

Due to the increased sensitivity in chemical analysis, man has become increasingly aware of toxic substances in his foods. This knowledge has led to self-imposed restrictions and governmental regulations on the use of pesticides and industrial chemicals throughout the world. State and federal programs which involve monitoring food products for contaminants have been instrumental in the enforcement of these regulations and in the identification of new potentially hazardous substances in foods (1). However, several food products that are produced and marketed by individuals at independent small businesses have not been monitored for chemical contaminants.

Apple cider is produced and marketed at numerous locations throughout the state of Connecticut. The purpose of this study was to analyze apple cider which was produced and sold at representative geographical regions of the state for elemental and pesticide contamination.

A thorough search of the literature has revealed no information on the environmental contamination of apple cider. A few studies were found that dealt with metal contamination of apples and other fruits (2,3,4). Most of these studies, however, were performed on samples grown outside the United States.

There are at least two possible causes of contamination to cider. The first source is from the apples used in cider production. Orchards are treated with various organophosphate, carbamate and organochlorine pesticides (5) which can be adsorbed by the fruits. Most of these compounds are very hydrophobic and only slightly water soluble. Since apple

cider consists mainly of the aqueous portion of the apple, it would seem unlikely that pesticides would be passed into the cider. However, most apple cider contains some pulp material which may carry dissolved pesticides in the pulp lipids.

Contamination of apple cider may also occur during the mechanical processing of the apples. Organic substances may be dissolved from lubricants while metals may be leached from metal storage containers by the acidic cider.

Our aim in the present study was to determine if any of these chemical substances exist in toxic concentrations in Connecticut-produced and marketed apple cider. In this pilot program cider samples representing all geographical regions of the state were collected and analyzed for the presence of metals and halogenated pesticides.

EXPERIMENTAL

Sample Collection: Duplicate one-half gallon bottles of cider were collected from mills or roadside stores representing the geographical areas of Connecticut that are listed on the map in Fig. 1. All samples were obtained during September of 1977 except samples YZ which were collected in September 1978.

Metal Analysis: Each sample of cider was inverted and shaken vigorously in the original container and then placed in an ultrasonic bath for 15 min. The sample was taken from the sonicator and inverted several times to insure homogeneity. A 50.0 mL sample of the cider was placed in a 100 mL beaker. The cider was evaporated to approximately 5 mL and 10.0 mL of nitric acid (Ultrex) were added. The solution was heated at approximately 80° until all of the nitric acid had evaporated. The solution was allowed to cool and 1 mL of nitric acid was added. The solution was quantitatively transferred to a 50.0 mL volumetric flask and then diluted to 50.0 mL with reagent grade water. The resulting solution was a dissolved, undiluted solution of the cider in 2.0% nitric acid.

Required dilutions of the dissolved cider samples were made with 2.0% nitric acid and analyzed for Fe, Zn, Mg and Mn by flame atomic absorption. A one-fourth dilution of the sample was made with reagent grade water to make the solution 0.5% in nitric acid. Appropriate dilutions of this solution were made with 0.5% nitric acid and analyzed for Cu, Pb and As by flameless atomic absorption using a graphite furnace (Perkin-Elmer Model

2200). The analyses were performed on a Perkin-Elmer Model 403 atomic absorption spectrometer and the parameters used were optimized around those recommended in the instrument's analytical manual (6).

Screen for Halogenated Hydrocarbons: Ten mL of cider, mixed by ultrasonification as described for the metal analysis, were placed in a 15 mL culture tube. Five mL of hexane (Burdick and Jackson) were added and the solution was mixed on a rotorack mixer for 10 min. The organic layer was decanted into a centrifuge tube and another 5 mL of hexane was added to the cider. The solution was again mixed on a rotorack mixer for 10 min. The second hexane extract was combined with the first and the total was evaporated to 1 mL in a 3 ball Snider evaporator. Five mL of the concentrated extract were analyzed by gas-liquid chromatography. A Perkin-Elmer Model 3920B gas chromatograph with a 6' glass column of 3% OV-17 on Chromosorb W-HP with a column temperature of 200°, and injector temperature of 215° and a carrier gas of 5% methane/argon at a flow rate of 30 mL/min was used. A Ni^{63} electron capture detector at 275° was used to detect halogenated compounds. The standing current was set at 3.0 and the attenuation at 32.

RESULTS AND DISCUSSION

The map in Fig. 1 shows the locations where the apple cider samples were collected. The concentrations of Cu, Fe, Zn, Mg, Mn and Pb in the respective cider samples are listed in Table I. In addition, As was not present in any of the samples at a concentration greater than 0.010 μg/mL.

The significance of these results was difficult to evaluate. Information on "normal" metal concentrations in cider could not be found in the literature. A few studies have been reported which list metal concentrations in whole apples (7,8,9). Table II summarizes these data for apples grown at different locations in the United States. Since the concentrations were calculated on a wet weight basis the values may be compared directly to the respective metal concentrations listed in Table I. Most of the metals were slightly more concentrated in the cider than in whole apples. This would be expected if the majority of the metal is located in the aqueous portion of the apple. During analysis of the whole apple the solid portion would add weight without contributing metal to the sample. The result would be a diluting effect when compared to a similar analysis of the aqueous portion alone. These data suggested that the average cider concentrations of Cu,

TABLE I. Concentrations of Metals in Cider Marketed in Connecticut.

Sample[a]	Date Collected	Metal Concentration (μg/mL)					
		Cu	**Fe**	**Zn**	**Mg**	**Mn**	**Pb**
AB	9/13/77	0.48	2.37	0.167	30.3	0.174	0.021
CD	9/13/77	0.46	1.48	0.107	37.0	0.142	0.030
EF	9/20/77	0.24	0.70	0.093	21.3	0.026	0.047
GH	9/20/77	0.37	0.56	0 115	27.0	0.165	0.090
IJ	9/20/77	0.41	1.57	0.041	20.2	0.073	0.040
KL	9/27/77	0.73	2.03	0.255	32.6	0.175	0.029
MN	9/27/77	0.46	4.51	0.154	34.0	0.225	0.077
OP	9/27/77	3.03	13.63	0.769	48.3	0.357	0.130
QR	9/28/77	0.40	0.94	0.488	43.8	0.239	0.032
ST	9/28/77	0.38	1.14	0.131	41.5	0.255	0.025
UV	9/28/77	0.48	5.77	0.799	39.0	0.286	0.142
X[b]	9/28/77	0.69	4.81	0.172	38.4	0.312	0.189
Average		0.68	3.29	0.274	34.5	0.202	0.071
Standard Deviation		0.75	3.69	0.264	8.7	0.096	0.056

[a]*See Fig. 1 for the collection location of the samples.*

[b]*The pair to this sample was lost after collection so that this sample represents only one sample from this location.*

TABLE II. Concentration of Metals in Apples

Reference	#	Metal Concentrations (μg/mL)				
		Cu	**Fe**	**Zn**	**Mg**	**Mn**
Upshaw, *et. al.* (1978)	7	0.37-0.43	1.1-1.3	0.53-0.67	26.2-29.4	0.27-0.33
Zook & Lehmann (1968)	8	0.16-0.40	0.40-0.93	—	26.0-35.0	0.10-0.38
Haller, *et. al.* (1968)	9	0.3	2.1	—	—	0.3

Fe, Zn, Mg and Mn were well within the "normal" range. No information was found on normal concentrations of arsenic in apples; however, the allowable concentration of arsenic in public water supplies is 0.05 μg/mL (10). The average concentration of this metal in the cider samples was well below this level.

In England the Lead in Food Regulations (1961) set an upper limit of 3 μg/mL for Pb in undried apples (11). The levels of Pb in the cider samples examined were less than one-tenth of this acceptable limit.

Except for one set of samples, the concentration of the respective metals in individual cider samples were within 2 standard deviations of the mean concentration. In sample OP the Cu concentration was 4.5 times the mean and the Fe concentration was 4.1 times the mean. Both of these levels represent a value greater than 3 standard deviations of the respective mean concentration. A second set of cider samples (YZ) was collected from this location one year after the first. The average Cu and Fe concentrations of these samples were 2.80 and 11.10 μg/mL, respectively. These data suggested that cider at location OP was contaminated from an external source with Cu and Fe.

Calves liver is considered to be a rich dietary source of both Cu and Fe. The concentration of Cu in liver is 44 μg/gm (12) whereas the concentration of Fe in liver is 80 μg/gm (13). Since the concentrations of Cu and Fe in cider sample OP were well below the normal concentrations of these metals in other foods, it may be concluded that they were not at toxic or hazardous concentrations.

The samples listed in Table I were also screened for the presence of common halogenated pesticides. These compounds were not detected at a level greater than the detection limit of approximately 50 μg/mL.

CONCLUSION

The concentrations of Cu, Fe, Zn, Mg, Mn, Pb and As in apple cider were found to be well below toxic or hazardous concentrations in a representative set of samples collected in Connecticut. Comparison with the concentration of the respective element in whole apples suggests that the metal concentrations in apple cider (tested in this study) can be considered normal concentrations. The cider samples were also found to be free of hazardous halogenated pesticides. Future studies will examine the concentrations of the slightly water soluble organophosphates and carbamates in apple cider.

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