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EVALUATION OF ANTIMONY, CADMIUM AND LEAD LEVELS IN VEGETABLES, DRINKING AND RAW WATER FROM DIFFERENT AGRICULTURAL AREAS*

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Lead and cadmium levels in edible vegetables and antimony, lead and cadmium in drinking and raw waters from three agricultural areas exposed to different levels of environmental pollution (1—high industrial pollution, 2—high urban pollution, 3—standard low industrial and urban pollution) are determined.

The organic matter is destroyed by repeated attack with nitric acid. Cadmium and lead are determined by graphite furnace atomic absorption spectrometry (GFAAS) and antimony by hydride generation atomic absorption spectrometry (HGAAS).

When the results obtained for three different areas are compared, differences between cadmium and lead contents in vegetables are observed. Waters are not contaminated with antimony, cadmium or lead in any area.

KEY WORDS: Contaminants, sampling, vegetables, water, atmosphere, graphite furnace atomic absorption spectrometry, hydride generation atomic absorption spectrometry, antimony, cadmium, lead, field studies.

INTRODUCTION

People who are not exposed in their work to environmental trace element contamination nevertheless come into contact with these pollutants through the contamination of the foods and water they ingest.

Lead and cadmium are well-known environmental pollutants and have been widely studied in the past few years. Good analytical techniques are available for measuring these elements in foods and waters. They are sensitive enough to detect the low levels present in foods and also the possible increases as a result of contamination.

Very few data, however, are available for antimony in the environment because the earth's crust contains only very small amounts of this element and because of

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the problems involved in measuring it at the levels of ng/g present in waters and foods.

In areas close to heavily travelled thoroughfares, lead concentration in the atmosphere¹ ranges between 0.4 and 7.6 $\mu\text{g}/\text{m}^3$, which is far higher than the values obtained in non-industrialized rural areas,² where the concentrations rarely exceed 2.5 $\mu\text{g}/\text{m}^3$. Most of the environmental lead comes from the use of leaded gasoline. Because of it, crops and the water used for irrigation in polluted areas may be contaminated.

Cadmium levels in the atmosphere³ are very low when compared with those of lead. They range from N.D. to 0.06 $\mu\text{g}/\text{m}^3$. This element occurs in vegetables as a result of both the quantities present in fertilizers (phosphatic fertilizers contain high concentrations of cadmium⁴) and the deposition from the atmosphere on vegetables growing near sources of cadmium emissions, such as smelters.⁵

Antimony enters the aquatic environment as a result of the erosion of rocks, through effluents from mining and manufacturing (textile, rubber and ceramics), and from municipal discharges. Antimony levels in tap waters range from N.D. to 10 $\mu\text{g}/\text{l}$, which is the limit set by the EEC in drinking water.^{6,7} Foods and water are the most important sources of antimony.

Lead and cadmium toxicity is well-known today. Although antimony has no known function in living organisms and is not one of the most toxic elements,⁸ antimony and its compounds have been considered priority pollutants by the Environmental Protection Agency.⁹

It is, therefore of interest to know the influence of environmental contamination on antimony, cadmium and lead level in waters and foods, especially those of vegetal origin.

Extremely sensitive analytical methods such as GFAAS for lead and cadmium and HGAAS for antimony are needed to measure the lead, cadmium and antimony levels usually present in foods and waters.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Model 2380 atomic absorption spectrophotometer, equipped with antimony, cadmium and lead hollow cathode lamps and a deuterium lamp for background correction.

Cadmium and lead: a Perkin-Elmer graphite furnace, Model HGA-400, and a Kipp and Zonnen Model BD40 strip-chart recorder are used.

Argon of 99.9998% purity is used as the purging gas through the graphite tube. Solutions are transferred with Brand fixed-volume micropipettes.

Antimony: a one-necked 100 ml reaction flask connected to a gas inlet-outlet adapter is used. The outlet tube of the adapter is connected to an open-ended flame-heated silica tube where the hydrides are atomized.

A Kipp and Zonnen Model BD40 strip-chart recorder is used. A peristaltic pump is adapted for the sodium borohydride solution addition.

Reagents

All reagents are of analytical grade unless otherwise stated.

Distilled-deionized water is used throughout.

Hydrochloric acid (sp. gr. 1.33)

Nitric acid (sp. gr. 1.1)

Potassium iodide 2% P/V

Ascorbic acid 2% P/V

Sodium borohydride 3% P/V

Sodium hydroxide 2% P/V

Antimony stock solution (1000 µg/ml): Titrisol® 1.8744 g SbCl₃ in 1000 ml of HCl 24%.

Cadmium stock solution (1000 µg/ml): 1.8546 g Cd(SO₄)₂ are dissolved in water and completed to 1 L.

Lead stock solution (1000 µg/ml): 1.5984 g Pb(NO₃)₂ are dissolved in water and completed to 1 L.

Working standard solutions are prepared from stock solutions by dilution with distilled-deionized water.

Contamination Control

All glass and polyethylene ware are soaked in 10% (V/V) nitric acid for 24 h and rinsed with distilled-deionized water before use. Pipette tips are cleaned before use by first pipetting with 10% (V/V) nitric acid and then with distilled-deionized water.

Sampling

Samples of edible vegetables and raw waters are taken from three agricultural areas exposed to different degrees of environmental pollution.

The areas are:

1. High industrial pollution.
2. High urban pollution.
3. Standard low industrial and urban pollution.

The vegetables and fruits analyzed are: artichokes, broad beans, red cabbage, carrots, chard, lettuce, thistles and oranges.

Number of samples analyzed: the first problem is to ascertain the number of samples that should be analyzed to obtain a good estimate of the cadmium and lead content present in the vegetables and the best way to do the sampling. The number of samples that should be taken are estimated by applying the following mathematical expression¹⁰ to the results obtained in a previous analysis of six samples representing the different types of vegetables analyzed.

$$10\% \bar{x} = t_{n-1} \frac{s_{n-1}}{n^{1/2}}$$

Where:

\bar{x} = mean concentration of antimony, cadmium and lead present.

t_{n-1} = Student *t* at a probability level of 95%.

S_{n-1} = standard deviation.

n = number of samples that should be taken.

In the case of some samples the value *n* is very high and the analysis of such a large number of samples is far beyond the possibilities of our laboratory. Therefore, and in order to standardize the number of samples to be analyzed, it was decided that 10 samples of each vegetable should be taken.

Ten samples of 8 types of vegetables are analyzed. Three water samples of each area should be taken, twenty-seven determinations for each element from the three areas are taken in all. The antimony, cadmium and lead content of the samples is measured.

Preparation and Preservation of Samples

Only edible parts of the vegetables are analyzed. The vegetables are washed and cut and the roots and leaves are removed. The fruits are peeled and their seeds removed. Perishable foods are kept in a refrigerator at 5°C until testing.

When the water samples are collected, nitric acid is added (final concentration 0.2%) and the water is stored in a refrigerator at 5°C until testing.

Determination

1. Sample digestion: repeated nitric acid procedure.¹¹ Waters are not mineralized.

2. Analytical methods:

– GFAAS method

Direct determination in the digested solution with instrumental conditions of Tables 1 and 2.

– HGAAS method

100 ml of water samples are first evaporated to dryness in a sand bath. The residue is dissolved with 10 ml hydrochloric acid 1.75% V/V and is placed in the reaction flask. 1 ml of the prereductant solution (potassium iodide 2% W/V + ascorbic acid 2% W/V) is added and the reaction flask is kept in the dark for five minutes to allow the Sb(V) to be reduced to Sb(III). The reaction flask is then connected to the adapter and the reductant solution (sodium borohydride 3% W/V + sodium hydroxide 1% W/V) is added through a peristaltic pump at a rate of 15 ml/min until the peak reaches its maximum absorption (height). Instrumental conditions in Table 1.

RESULTS AND DISCUSSION

Tables 3 and 4 show the cadmium and lead content, respectively, of all the fruits and vegetables grown in the areas under study.

Table 1 Recommended atomic absorption spectrometer settings

	<i>Antimony^a</i>	<i>Cadmium^b</i>	<i>Lead^b</i>
Wavelength (nm)	217.6	228.8	283.3
Slit width (nm)	0.7	0.7	0.7
Lamp current (mA)	20	4	10
Sample volume (ml)	10	0.01	0.01
Air flow (L/min)	13		
Acetylene flow (L/min)	1.2		
Argon:			
purge flow (L/min)	1.5		
analytical flow (L/min)	0.4	mini-flow	
Chart speed (mm/min)	5	5	5

Atomic absorption spectrometer Perkin Elmer 2380; Kipp and Zonnen Model BD40 strip-chart recorder.
Antimony, cadmium and lead hollow cathode lamps.

^aHydride Generation^bGraphite Furnace HGA-400**Table 2** Recommended furnace programmer settings

	<i>Cadmium</i>	<i>Lead</i>
<i>Dry:</i>		
Temperature (°C)	110	130
Ramp time (s)	5	5
Hold time (s)	10	10
<i>Char:</i>		
Temperature (°C)	500	500
Ramp time (s)	5	5
Hold time (s)	15	15
<i>Atomisation:</i>		
Temperature (°C)	2000	2300
Ramp time (s)	2	2
Hold time (s)	5	5
<i>Clean:</i>		
Temperature (°C)	2600	2600
Ramp time (s)	1	1
Hold time (s)	1	1

Peak height mode; deuterium arc; mini flow.

The average cadmium and lead content in chard, artichokes and carrots (the vegetable species that are grown simultaneously in the three areas) are indicated here in histograms in order to facilitate comparison (Figure 1—cadmium; Figure 2—lead).

The cadmium and lead contents of the vegetables grown in the three agricultural areas studied are compared by variance analysis (ANOVA), and Tuckey test,¹² in order to detect possible significant differences. See Tables 5 and 6.

The results obtained from comparing of the mean contents of cadmium and lead in vegetables grown in the three agricultural areas show that:

Table 3 Cadmium content (ng/g) in fruits and vegetables

	Area 1 ^a	Area 2 ^a	Area 3 ^a
Carrots	12.57 ± 5.55	3.21 ± 1.27	4.96 ± 0.62
Artichokes	14.33 ± 6.46	2.48 ± 1.55	10.17 ± 2.53
Chard	16.51 ± 8.68	38.19 ± 22.31	7.09 ± 0.94
Thistles	8.75 ± 1.08	18.96 ± 11.88	
Red cabbage	3.50 ± 0.72	1.80 ± 0.06	
Lettuce	85.44 ± 10.82	16.16 ± 14.85	
Broad beans	N.D.		N.D.
Oranges	N.D.	N.D.	2.29 ± 1.25

N.D. = Not Detectable

$$^a \bar{x} \pm t_n \cdot \frac{S_n - 1}{n^{1/2}}$$

Table 4 Lead content (ng/g) of fruits and vegetables

	Area 1 ^a	Area 2 ^a	Area 3 ^a
Carrots	159.04 ± 84.45	132.09 ± 25.26	74.89 ± 11.51
Artichokes	70.24 ± 45.38	200.40 ± 120.59	N.D.
Chard	390.12 ± 72.91	304.26 ± 26.51	220.34 ± 60.91
Thistles	38.15 ± 12.32	165.17 ± 32.34	
Red cabbage	14.72 ± 4.21	N.D.	
Lettuce	935.74 ± 112.86	256.88 ± 86.33	
Broad beans	150.51 ± 18.41		86.76 ± 8.87
Oranges	N.D.	N.D.	N.D.

N.D. = Not Detectable

$$^a \bar{x} \pm t_n \cdot \frac{S_n - 1}{n^{1/2}}$$

—The lead contents of vegetables coming from area 3, which can be considered standard and are relatively free from contamination, are considerably lower than in the vegetables grown in areas 1 and 2.

—The application variance analysis makes it clear that: the lead content of leafy vegetables (chard) are significantly different in three areas studied. Significant differences are found between areas 1 and 2, 2 and 3 and 1 and 3. Lead content is higher in chard grown in area 1 than in area 2 and higher than in the vegetables coming from area 3.

—In the case of carrots the differences are obtained when vegetables grown in areas 1 and 2 are compared with the ones grown in area 3.

—In artichokes, however, probably because the external parts of the inflorescence are eliminated before doing the analysis, no significant differences can be found.

—The cadmium content of vegetables are several times lower than the lead content of the same vegetables.

—There are significant differences in the cadmium content of the same vegetables when they are cultivated in areas with different degrees of contamination. But no single area yields vegetables with a consistently higher content, in some species the content is higher in vegetables from area 1, while in others in area 2 or 3. Therefore it is not possible to come to a general conclusion as to the influence of the degree of contamination in cadmium content of vegetables.

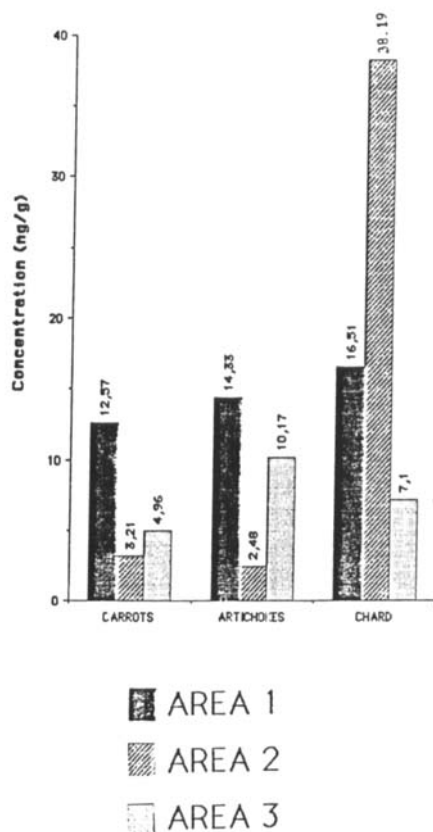


Figure 1 Cadmium content (ng/g) in vegetables

The antimony, cadmium and lead content in irrigation waters are shown in Table 7. Cadmium and lead content of the irrigation waters analyzed are below the maximum acceptable levels in drinking water. There are no significant differences between the three areas. Therefore, waters are not contaminated with cadmium and lead and they will have no influence on the content in vegetables.

CONCLUSIONS

—The degree of pollution in the three different areas studied significantly influenced the lead content of the vegetables grown there. The results obtained (especially those referring to leafy vegetables) confirm the hypothesis of aerial deposition of the element (lead).

—Cadmium content varies significantly in a given vegetable depending on the area in which it is grown. There is, however, no single area that produces higher levels than the other areas for all the vegetables. It must be emphasized that cadmium contamination, generally produced by industries, is not related to traffic, and that cadmium is absorbed by the roots. Further studies of soils and fertilizers are needed to complete the present work and reach firm conclusions.

—Irrigation water in the areas studied are not contaminated with antimony,

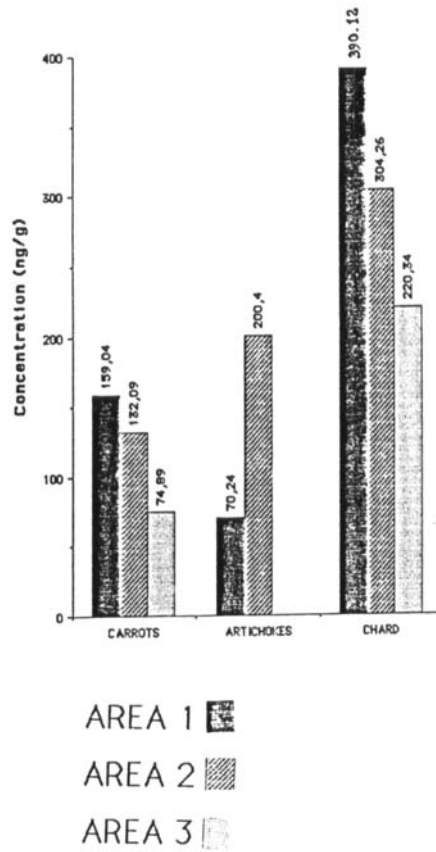


Figure 2 Lead content (ng/g) in vegetables

Table 5 Results of analysis of variance (ANOVA)

Matrix	Lead		Cadmium	
	F	Ft	F	Ft
Artichokes	2.27	10.56N.S.	25.18	8.86*
Carrots	12.71	6.23*	35.81	6.11*
Chard	12.59	5.57*	9.14	4.94*

F = Ratio of mean square/residual mean square

Ft = Table value

*Significatives differences at probability of level of 0.01

N.S. = Differences not significatives

cadmium and lead. The contents observed are below the maximum accepted values for drinking water.¹³

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Table 6 Results of Tuckey test

	<i>Artichokes</i>	<i>Carrots</i>	<i>Chard</i>
<i>Lead:</i>			
Area 1-2	N.S.	N.S.	a
Area 1-3		b	b
Area 2-3		b	a
<i>Cadmium:</i>			
Area 1-2		b	b
Area 1-3		b	N.S.
Area 2-3	b	N.S.	b

*Significatives differences at probability level of 0.05

*Significatives differences at probability level of 0.01

N.S. = Differences not significatives

Table 7 Antimony, cadmium and lead contents ($\mu\text{g/l}$) in waters of three areas

	<i>Antimony</i>	<i>Cadmium</i>	<i>Lead</i>
<i>Area 1:</i>			
Sample No. 1	0.45	1.18	10
Sample No. 2	0.26	1	10
Sample No. 3	0.39	1	16.73
<i>Area 2:</i>			
Sample No. 1	0.72	1	10
Sample No. 2	0.47	1	10
Sample No. 3	0.77	1	54.47
<i>Area 3:</i>			
Sample No. 1	0.30	1	32.18
Sample No. 2	0.05	1	14.35
Sample No. 3	0.08	1	10
Maximum limit	10	5	50

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