

DETERMINATION OF LEAD AND CADMIUM IN VINEYARD SOILS, GRAPES AND WINES OF THE AZORES

DÉTERMINATION DES TENEURS EN PLOMB ET EN CADMIUM DES SOLS DES VIGNOBLES, DES RAISINS ET DES VINS DES AÇORES

M.T. RIBERO de LIMA¹, M.T. CABANIS², L. MATOS¹,
Genyvie CASSANAS³, M.T. KELLY^{2*} and A. BLAISE²

1: Departamento de Ciencias Agraria, Universidade dos Açores,
9700 Angra do Heroísmo, Tereira, Azores

2: Centre de Formation et de Recherche en Œnologie, Faculté de Pharmacie,
15 Avenue Charles Flahault, BP 14,491, 34093 Montpellier Cedex 5, France

3: Laboratoire de Physique Industrielle et traitement de l'Information, Faculté de Pharmacie,
15 Avenue Charles Flahault, BP 14,491, 34093 Montpellier Cedex 5, France

Abstract: This study describes the determination of lead and cadmium in vineyard soils of three regions of the Azores, and in the grapes and wines produced in those regions. The elements were analysed by graphite furnace atomic absorption spectrometry (GFAAS); wines were analysed without prior sample pre-treatment; grapes and soils were analysed after microwave digestion. Soils were also analysed by an alternative technique in order to establish the soluble fraction of these minerals directly assimilable by the plant. Statistical analysis revealed that the amounts of these minerals in wines are 28 µg/l and 0.58 µg/l for lead and cadmium, respectively. The levels of pollution by these elements is significantly lower in the Azores by comparison with other regions (according to literature values).

Résumé : Cette étude porte sur la recherche de deux polluants dans les vins des Açores : le plomb et le cadmium. Ces éléments traces sont toxiques et peuvent engendrer des maladies chroniques graves. L'OIV a fixé des concentrations limites pour ces minéraux : cadmium 0,01 mg/l et plomb 0,2 mg/l dans le vin. Les Iles des Açores sont situées au milieu de l'océan Atlantique et nous avons estimé qu'il serait intéressant de déterminer la teneur de ces éléments dans les sols, raisins et vins de ces régions afin de connaître leur degré de pollution. Les dosages ont été réalisés par absorption atomique en four, en utilisant un modificateur de matrice ; la méthode a été vérifiée en analysant un matériel de référence certifié. Le vin a été analysé directement et les raisins et les sols ont subi une minéralisation au micro-onde au préalable. La proportion des minéraux sous forme libre dans le sol a été déterminée par une technique de complexation à l'EDTA. Les teneurs de plomb et cadmium sont nettement en dessous les teneurs limites, avec une moyenne de 28 µg/l pour le Pb et de 0,58 µg/l pour le Cd. Par rapport à d'autres régions semblables, les Iles Canaries, par exemple ou encore le continent européen, on en conclut que les Iles des Açores sont relativement peu polluées.

Key words: lead, cadmium, soil, grapes, wine, atomic absorption, vineyard, pollution

Mots clés : éléments traces, plomb, cadmium, vin raisin, sol, minéralisation micro-ondes, absorption atomique, vignoble, pollution

INTRODUCTION

Cadmium and more especially, lead, have been present in reasonably high concentrations due to the spread of industrialisation. Lead, in fact is amongst the most widespread metals on earth; cadmium is less abundant but is found in almost all zinc ores and often in the sea-water of highly polluted ports (ROHLEDER and KORTE, 1982). Furthermore, the presence of these two elements is stron-

gly indicative of industrial pollution which is particularly serious in view of the fact it occurs in the atmosphere.

Both of these elements are toxic to man, producing more frequently a chronic toxic syndrome, as has been outlined by the Public Health Council of France (CABANIS, 1985) and by the FDA in the United States. These elements are cumulatively toxic and enter the body principally via two mechanisms, the lungs by inhalation and absorption by the gastrointestinal tract. On account

Table I - Temperature program for the analysis of lead by GFAAS**Programme du four graphite pour le plomb**

Step	Temp. (°C)	Duration (s)	Gas flow (l/min)	Measure
1	75	2.0	3.0	
2	95	20.0	3.0	
3	140	15.0	3.0	
4	300	8.0	3.0	
5	450	7.0	3.0	
6	480	10.0	3.0	
7	900	20.0	3.0	
8	900	1.0	0	
9	2250	0.7	0	on
10	2250	1.0	0	on
11	2250	2.0	3.0	

of their toxicity, the Office Internationale de la Vigne et du Vin (OIV) proposed limits of 10 µg/l and 200 µg/l for cadmium and lead, respectively, in wine.

The Azores archipelago constitutes a group of small islands situated in the Atlantic ocean, 1400 Km from the Portuguese capital, Lisbon. The islands are situated in area ocean where American and African tectonic plates meet and thus the soil is predominantly volcanic, which is another particularity of the region. Due to their isolated position in the Atlantic ocean, and their distance from industrial centres, it is to be expected that the soil of the Azores would contain very low levels of lead and cadmium since these elements are highly indicative of environmental pollution. It was also considered of interest to compare the amounts found in the soils with those found in the finished wine, and therefore lead and cadmium were determined in the soils, grapes and wines of the principal viticultural regions of the Azores, which are situated in the islands of Terceira (Biscoitos region), Pico and Graciosa.

MATERIALS AND METHODES

All chemicals and reagents were obtained from Carlo Erba and were of analytical grade or equivalent.

I - GRAPHITE FURNACE (GFAAS)

GFAAS determinations were carried out on a Varian (Varian Techtron Pty, Ltd., Mulgrave, Australia) series AA-1275 AA spectrophotometer equipped with a deuterium lamp and a Varian series GTA 95 electrothermal cell.

For lead determinations, the hollow cathode lamp had a wavelength of emission of 283.3 nm, the slit was set at 0.5 nm, the current at 5 mA. The oven temperature program is presented in table I. For cadmium, the hollow cathode lamp had a wavelength of emission of 228.8 nm, the slit was set at 0.5 nm, the current at 4 mA. The oven

temperature program is presented in table II. In both cases, the injection temperature was 70°C, nitrogen was used as the purge gas, the ovens were of pyrolytic graphite. Measurements were based on peak heights, and a deuterium lamp was used for background correction.

II - ASHING

The automated microwave digestion apparatus used was a Maxidigest Mx3250 supplied by Prolabo (France). Depending on the matrix, two different programs of the same duration (29 minutes) were used for grapes (table III) and for soil (table IV). Grapes were rinsed in water and the stalks removed before crushing. Digested samples of berry must (15 g) or soil (5 g) were brought to final volume of 50 ml.

III - EDTA EXTRACTION

The percentage of soluble elements in the soils was obtained by EDTA extraction and the results compared to the total content determined by atomic absorption spectrophotometry after ashing. The EDTA solution was prepared by dissolving 14.6 g EDTA in 950 ml doubly distilled water containing 8 ml of 35 % ammonia. The pH was adjusted to 7 and the solution was made up to 1 l. Soil (10 g) was added to 50 ml of this solution and mixed by magnetic stirring at 125 rpm for 60 minutes.

IV - CALIBRATION AND QUANTITATION

A calibration curve (5-20 µg/l) lead was prepared by appropriate dilution of a stock solution of lead nitrate (equivalent to 1 g/l lead). Both calibration standards and the samples were prepared in a solution of 1% NH₄H₂PO₄ in 1% nitric acid as matrix modifier. A total volume of 20 µl standard or 10 µl sample solution plus 10 µl modifier were injected into the oven.

A calibration curve for cadmium (0.25-1.5 µg/l) was prepared by appropriate dilution of a stock solution of cad-

Table II - Temperature program for the analysis of cadmium by GFAAS
Programme du four graphite pour le cadmium

Step	Temp. (°C)	Duration (s)	Gas flow (l/min)	Measure
1	75	2.0	3.0	
2	95	40.0	3.0	
3	140	15.0	3.0	
4	300	8.0	3.0	
5	450	7.0	3.0	
6	480	10.0	3.0	
7	900	20.0	3.0	
8	900	1.0	0	on
9	2000	1.1	0	on
10	2000	1.0	0	on
11	2000	2.0	3.0	

Table III - Ashing programme for grapes (TEISSEDRE *et al.*, 1993)
Programme pour la minéralisation des raisins (TEISSEDRE *et al.*, 1993)

Step	Reagent	Volume (ml)	Microwave power (%)	Time (min)
1	HNO ₃ , 65%	25	60	1
2		0	30	10
3	H ₂ O ₂ , 35%	3	15	3
4		3	40	15

Table IV - Ashing programme for soils (TEISSEDRE *et al.*, 1993)
Programme pour la minéralisation de la terre (TEISSEDRE *et al.*, 1993)

Step	Reagent	Volume (ml)	Microwave power (%)	Time (min)
1	HNO ₃ , 65%	20	60	1
2		0	30	10
3	H ₂ O ₂ , 35%	3	15	3
4		0	40	15

mium nitrate (equivalent to 1 g/l cadmium). Both calibration standards and the samples were prepared in a solution of 1% NH₄H₂PO₄ in 1% nitric acid as matrix modifier. A total volume of 20 µl standard or 5 µl sample solution plus 15 µl modifier was injected into the oven.

The method was applied to the analysis of a certified reference material (Tort-2, Lobster hepatopancreas for trace metals) supplied by the National Research Council of Canada. The certification specifies 0.35 ± 0.13 µg/g for lead and 26.7 ± 0.6 µg/g for cadmium; 0.37 and 31.1 µg/g were found for the two elements, respectively.

RESULTS AND DISCUSSION

The levels of lead and cadmium found in the different samples of soil, grapes and wines are presented in tables V and VI. Average results per region and per matrix are presented in figure 1. A univariate statistical study (tables VII and VIII) was carried out in order to determine the dis-

tribution of the two elements in the soils, grapes and wines on a per island basis.

It may be observed that the levels of both cadmium and lead are significantly different in the soils of the three regions, though the distribution per region is not the same for the two elements. There was no significant difference between the concentrations of total lead found in samples taken at the two different sampling depths in both the Pico (mean concentrations 3 mg/kg) and Graciosa (mean concentrations 7 mg/kg) regions, which indicates that the total lead concentration originates in soil itself. The concentrations of lead (mean values 14 mg/kg) found in the superficial layers of the soil of the Biscoitos region are considerably greater than those found in the other regions (twice as much as in Graciosa and almost four times as much as the concentrations found in Pico). This difference may possibly be attributed to the fact that there is greater urbanisation in Biscoitos therefore the higher levels of lead are due to environmental pollution.

Table V – levels of lead in the soils, grapes and wines of the viticultural regions of the Azores.
Teneurs en plomb Pb pour les échantillons de sols, raisins et vins des régions viticoles des Açores.

Region	Soil (mg/kg)			Grapes (µg/kg)			Wines (µg/l)		
	Total conc	Soluble content		Varieties	Amount found	Varieties	Amount found	Varieties	Amount found
	Depth 10-20 cm	Depth 20-40cm	Depth 10-20 cm	Depth 20-40cm	Varieties	Amount found	Varieties	Amount found	
Pico	1,46	2,45	0,92	1,02	Rio Grande (w)	nd ^c	Rio Grande (w)	33,55	
	1,79	2,86	1,70	1,08	Periquita (r)	6,42	Periquita (r)	19,02	
	1,83	2,97	1,08	0,62	Saborinho (r)	nd	Saborinho (r)	18,73	
	2,09	3,53	0,56	0,59	Generosa (w)	nd	Generosa (w)	29,26	
	6,91	4,20	1,28	0,96	Arinto (w)	8,63			
	2,10	2,39	0,51	1,71	Rufete (r)	3,72			
	4,98	5,83	1,16	1,73	Verdelho (w)	4,57	Verdelho (w)	25,36	
	9,82	4,30	1,20	1,22	C. Sauvignon (r)	4,21	C. Sauvignon (r)	20,79	
	2,35	6,33	1,21	2,20	Agronomica (r)	1,99	Agronomica (r)	16,55	
	0,87	2,46	1,06	1,26	Seara Nova (w)	nd	Seara Nova (w)	27,57	
					Verdelho (w)	4,01	*Verdelho (w)		
					Arinto (w)	11,43	Arinto (w)	3,18	
					Terrantês (w)	0,98	Terrantês (w)		
				Seara Nova (w)	13,06	*Seara Nova (w)			
				Generosa (w)	10,85	Generosa (w)	3,45		
				Rio Grande (w)	5,60	Rio Grande (w)			
				Agronomica (r)	1,10	*Agronomica (r)	5,55		
				Periquita (r)	3,55	Periquita (r)			
Terceira	Depth 15-20 cm			Depth 15-20 cm					
	13,25	-	3,04	-	Verdelho (w)	20,83	Verdelho (w)	10,27	
	15,88	-	5,14	-	Arinto (w)	9,52	Arinto (w)	24,71	
					Terrantês (w)	12,77	Terrantês (w)	9,10	
					-	-	-	3,92	
	17,07	-	3,31	-	Verdelho (w)	nd	Verdelho (w)	53,36	
	491,91	-	135,00	-	Verdelho (w)	nd	Verdelho (w)	69,61	
	9,47	-	1,60	-	Verdelho (w)	nd	*Verdelho (w)	73,23	
					Terrantês (w)	nd	Terrantês (w)		
					-	-	-		
Graciosa	Depth 20 cm			Depth 20 cm					
					*Arinto (w)	nd	*Arinto (w)		
					Verdelho (w) (ss)**		Verdelho (w) (ss)**	37,32	
	7,27	6,34	1,71	1,13	Boal (w)	nd	Boal (w)		
	7,87	5,79	2,66	1,38	Verdelho (w)	0,13	Terrantês (w)		
	11,28	9,65	2,45	2,42	Boal (w)	5,53			
					Terrantês (w)	2,15	*Arinto (w)		
					Verdelho (w) (oak)***		Verdelho (w) (oak)***	26,27	
					Boal (w)		Boal (w)		
					Terrantês (w)		Terrantês (w)		
				-	-	-			
				Boal (w)	nd				
6,06	5,33	1,21	1,17	Tália (w)	18,59				
8,01	4,27	1,05	0,92						

a - Depth ; w - white; r - red; c - nd - not detected ; * Blend of different varieties; ** Wine aged in stainless steel tanks; *** Wine aged in oak barrels

Table VI – Levels of cadmium in the soils, grapes and wines of the viticultural Regions of the Azores.
Teneurs en cadmium Cd pour les échantillons de sols, raisins et vins des régions viticoles des Açores.

Region	Soil (mg/kg)				Grapes (µg/kg)				Wines (µg/kg)					
	Total conc.		Soluble content		Amount found		Varieties		Amount found		Varieties		Amount found	
	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm	Depth 10-20 cm	Depth 20-40 cm
Pico	0,09	0,09	0,10	0,10	0,11	0,11	Rio Grande (w)	Rio Grande (w)	3,87	3,87	Rio Grande (w)	Rio Grande (w)	0,21	0,21
	0,03	0,10	0,04	0,04	0,14	0,14	Periquita (r)	Periquita (r)	3,56	3,56	Periquita (r)	Periquita (r)	0,03	0,03
	0,10	0,06	0,14	0,14	0,12	0,12	Saborinho (r)	Saborinho (r)	4,26	4,26	Saborinho (r)	Saborinho (r)	0,08	0,08
	0,04	0,06	0,08	0,08	0,12	0,12	Generosa (w)	Generosa (w)	4,67	4,67	Generosa (w)	Generosa (w)	0,18	0,18
	0,24	0,25	0,25	0,25	0,41	0,41	Arinto (w)	Arinto (w)	3,56	3,56	-	-	-	-
	0,02	0,05	0,07	0,07	0,12	0,12	Rufete (r)	Rufete (r)	3,39	3,39	-	-	-	-
	0,20	0,28	0,21	0,21	0,28	0,28	Verdelho (w)	Verdelho (w)	4,06	4,06	Verdelho (w)	Verdelho (w)	0,04	0,04
	0,20	0,20	0,20	0,20	0,23	0,23	C. sauvignon (r)	C. sauvignon (r)	3,00	3,00	C. Sauvignon (r)	C. Sauvignon (r)	0,02	0,02
	0,04	0,08	0,07	0,07	0,11	0,11	Agronómica (r)	Agronómica (r)	2,63	2,63	Agronómica (r)	Agronómica (r)	0,03	0,03
	0,02	0,06	0,04	0,04	0,09	0,09	Seara Nova (w)	Seara Nova (w)	4,19	4,19	Seara Nova (w)	Seara Nova (w)	0,28	0,28
							Verdelho (w)	Verdelho (w)	1,10	1,10	*Verdelho (w)	*Verdelho (w)		
							Arinto (w)	Arinto (w)	4,25	4,25	Arinto (w)	Arinto (w)	0,26	0,26
							Terrantês (w)	Terrantês (w)	3,76	3,76	Terrantês (w)	Terrantês (w)		
							Seara Nova (w)	Seara Nova (w)	3,12	3,12	*Seara Nova (w)	*Seara Nova (w)	0,22	0,22
						Generosa (w)	Generosa (w)	3,31	3,31	Generosa (w)	Generosa (w)			
						Rio Grande (w)	Rio Grande (w)	3,28	3,28	Rio Grande (w)	Rio Grande (w)			
						Agronómica (r)	Agronómica (r)	3,42	3,42	*Agronómica (r)	*Agronómica (r)	nd ^c	nd ^c	
						Periquita (r)	Periquita (r)	0,66	0,66	Periquita (r)	Periquita (r)			
Terceira-Biscoitos	Depth 15-20 cm				Depth 15-20 cm									
	0,27	-	0,18	0,18	-	-	Verdelho (w)	Verdelho (w)	3,53	3,53	Verdelho (w)	Verdelho (w)	0,22	0,22
	0,46	-	0,32	0,32	-	-	Arinto (w)	Arinto (w)	2,90	2,90	Arinto (w)	Arinto (w)	0,21	0,21
	17,07	-	3,31	3,31	-	-	Terrantês (w)	Terrantês (w)	3,68	3,68	Terrantês (w)	Terrantês (w)	0,60	0,60
	491,91	-	135,00	135,00	-	-	-	-	-	-	Periquita (r)	Periquita (r)	0,12	0,12
	0,22	-	0,21	0,21	-	-	Verdelho (w)	Verdelho (w)	5,23	5,23	Verdelho (w)	Verdelho (w)	0,56	0,56
	0,42	-	0,52	0,52	-	-	Verdelho (w)	Verdelho (w)	2,87	2,87	Verdelho (w)	Verdelho (w)	0,22	0,22
	0,25	-	0,23	0,23	-	-	Verdelho (w)	Verdelho (w)	3,00	3,00	*Verdelho (w)	*Verdelho (w)	0,28	0,28
							Terrantês (w)	Terrantês (w)	3,13	3,13	Terrantês (w)	Terrantês (w)	37,32	37,32
											*Arinto (w)	*Arinto (w)		
Graciosa	Depth 20 cm				Depth 20 cm				Depth 50 cm					
	3,07	3,09	1,40	1,40	1,60	1,60	Arinto (w)	Arinto (w)	4,29	4,29	Verdelho (w) (ss)**	Verdelho (w) (ss)**	1,32	1,32
	1,38	1,02	0,55	0,55	0,36	0,36	Verdelho (w)	Verdelho (w)	4,35	4,35	Boal (w)	Boal (w)		
	1,96	1,96	0,75	0,75	0,60	0,60	Boal (w)	Boal (w)	3,28	3,28	Terrantês (w)	Terrantês (w)		
							Terrantês (w)	Terrantês (w)	3,31	3,31	Verdelho (w) (oak)***	Verdelho (w) (oak)***	26,27	26,27
											*Arinto (w)	*Arinto (w)		
											Verdelho (w) (oak)***	Verdelho (w) (oak)***	1,31	1,31
											Boal (w)	Boal (w)		
	0,60	0,45	0,27	0,27	0,21	0,21	Boal (w)	Boal (w)	4,64	4,64	Terrantês (w)	Terrantês (w)	-	-
	0,14	0,89	0,34	0,34	0,35	0,35	Tália (w)	Tália (w)	3,94	3,94	-	-	-	-

a - Depth ; w - white; r - red; c - nd - not detected ; *Blend of different varieties; ** Wine aged in stainless steel tanks; ***Wine aged in oak barrels

Comparison of the concentrations of soluble lead in two different soil layers shows that for Pico, the mean concentration is 1.07 mg/kg on the surface and 1.24 mg/kg in the lower layer, giving a ratio between the two of 0.86. The mean soluble lead values for Graciosa at the same sampling depths are respectively, 1.82 mg/kg and 1.40 mg/kg giving a ratio of 1.29. These values are identical to those calculated for total lead (0.92 for Pico and 1.28 for Graciosa) thus proving the homogeneity of the soil composition in the absence of surface pollution. The mean soluble lead concentration of Biscoitos was

3.27 mg/kg which is well above the corresponding values for the other islands. Finally, if we consider the ratio of the mean soluble lead values to the total lead values for the same sampling depths, (calculated by comparing the results obtained with ashing and by EDTA extraction), it emerges that the ratios are 0.31 and 0.22 for the superficial layers of Pico and Graciosa, respectively; the corresponding values for the lower sampling depths are 0.33 and 0.22 respectively, proving that the levels of lead are homogeneous in the different soil layers and further proving the absence of pollution related to human activity in

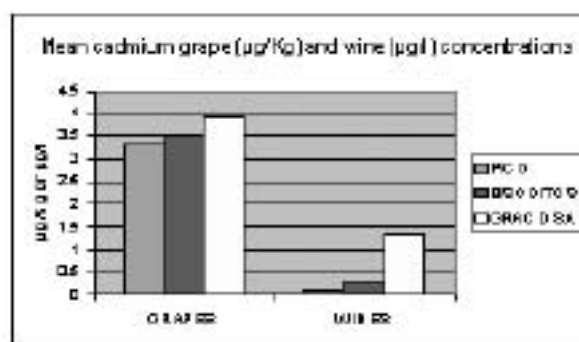
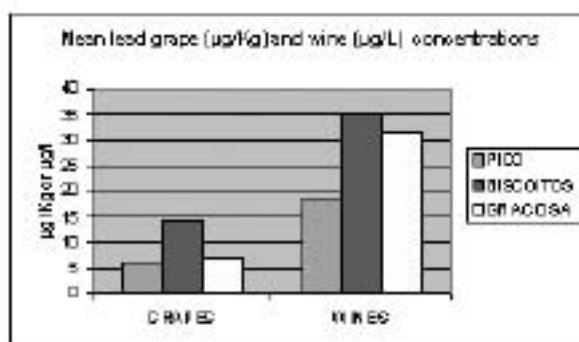
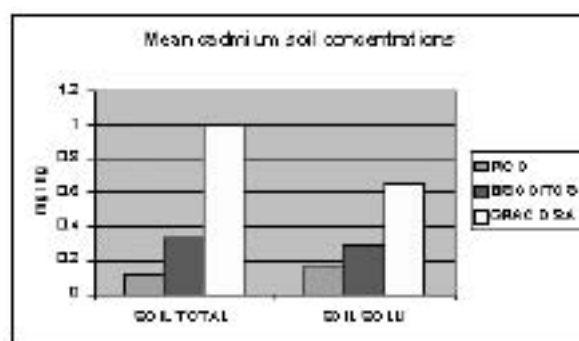
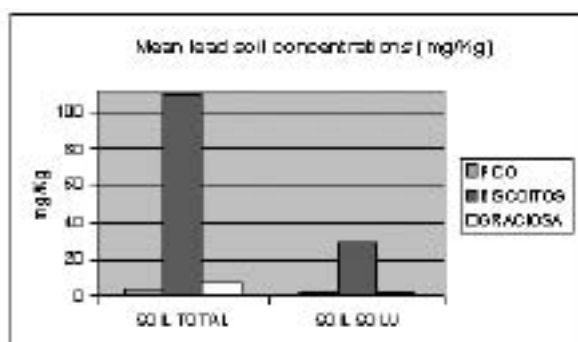


Figure 1a - Mean lead concentrations per region and per matrix

Figure 1b - Mean cadmium concentrations per region and per matrix

Teneurs moyennes pour le plomb par région et par matrice

Teneurs moyennes pour le cadmium par région et par matrice

Table VII - Statistical results for lead

Résultats statistiques pour le plomb

	Region	Pico	Biscoitos	Graciosa	P
	N° of samples	20	5	10	
Total soil	m	3.57	109.52	7.18	0.04
Content mg/Kg	esm	0.50	95.61	0.67	
Solubilized	m	1.15	29.61	1.61	0.05
soil content mg/Kg	esm	0.10	26.35	0.21	
	N° of samples	18	7	6	
Grapes	m	5.73	14.37	6.60	0.05
µg/Kg	esm	0.91	2.20	3.38	
	N° of samples	11	7	2	
Wines	m	18.45	34.88	31.79	0.23
µg/l	esm	3.17	11.28	5.52	

Table VIII - Statistical results for cadmium
Résultats statistiques pour le cadmium

	Region	Pico	Bischoitos	Graciosa	P
	N° of samples	20	5	10	
Total soil	m	0.11	0.32	1.45	<10 ⁻⁴
Content mg/Kg	esm	0.02	0.05	0.33	
Solubilized	m	0.15	0.29	0.64	<10 ⁻³
Soil content mg/Kg	esm	0.02	0.06	0.15	
	N° of samples	18	7	6	
Grapes	m	3.33	3.47	3.96	0.36
µg/Kg	esm	0.24	0.32	0.23	
	N° of samples	11	7	2	
Wines	0.1	0.13	0.32	1.32	0
µg/l	esm	0.03	0.07	0.01	

m: mean; esm: standard error; p: level of significance

these two islands. In the Bischoitos region, the ratio of the means of total and soluble lead is 0.23, however it was not possible to draw any conclusions with regards to pollution, even though the absolute levels of lead in this region are significantly greater than in the other islands.

The cadmium concentrations are in general considerably lower (5 to 30 fold) than the lead concentrations. Nonetheless, there are differences in the mean concentrations of this element between the three islands. The mean levels in the Pico region are of the order of 0.10 mg/kg of soil irrespective of the sampling depth and the form in which cadmium is present. Like the Pico region, the concentrations at both soil sampling depths are similar in the Bischoitos region, though in this case the concentrations are three times higher. It is likely that the majority of the cadmium occurs in the soil in the form of a soluble carbonate, zinc carbonate, for example, and that lead principally occurs as insoluble lead sulphide. Therefore if we assume that all the cadmium is present as this soluble carbonate, the quantities likely to be assimilated by the plant and to appear in the various organs of the vine will be greater than for lead.

Samples taken from similar sampling depths in Graciosa contain different amounts of cadmium, with values varying from factors of 1 to 20 in the extreme cases, however, the mean values for the surface layer and the layer immediately beneath are the same for each of the forms of cadmium. In this region, the ratio of soluble cadmium to total cadmium is 0.44, whereas the ratio was approximately 1 for the other islands. It is possible that this difference arises from the presence of naturally-occurring forms of cadmium that are not extractable by EDTA. These results would appear to indicate that the volcanic soil of the Azores permits plants to assimilate greater amounts (in terms of relative values) of cadmium than lead.

It is interesting to note from figure 1 that the relative concentrations of cadmium in the three regions (Graciosa > Bischoitos > Pico) is maintained from soil (total and soluble) to grapes to wines. Results are more variable for lead though the high concentration of this element in the soil of Bischoitos is reflected in the fact the wines and grapes of this region also have higher lead concentrations than the other two regions.

It should be noted, however, it would be very difficult at this stage of the analysis to distinguish naturally-occurring lead and cadmium from that arising from contamination resulting from environmental pollution. This is particularly true in view of the fact that these metals occur in more reactive forms in the atmosphere than naturally-occurring metals which frequently are found in forms that are relatively inert chemically. It has been shown that the distinction can be made between metals arising from contamination and those forming part of the natural pedo-geochemical composition of a given area. (BAIZE, 1997). Since this work involved the interpretation of the total trace metal content of soils, the author was able to establish alert levels above which more detailed studies would be required. For lead, he recommended that this level be set at 60 mg/Kg, and 0.7 mg/Kg for cadmium. Based on these values, only one region of the Azores (Graciosa, total cadmium soil concentration 1.45 mg/kg) may warrant monitoring for pollution or further investigation of natural composition of volcanic soils.

In grapes, the concentration of these elements are in the µg/kg range, whereas soil contains mg/kg concentrations. The levels of lead in grapes are higher in Bischoitos which corresponds to the fact that it has the highest soil lead concentrations of the three regions. The grape lead concentration of the two other regions are significantly lower and almost identical to one another. The cadmium

concentrations (3-4 µg/kg) in the grapes from the three areas are very similar and do not reflect the differences in soil concentrations. Like many other plants, the vine has the capacity to absorb relatively large quantities of toxic elements, without, however, any manifestation of plant toxicity since the metals are complexed by biomolecules contained within the plant. The vine, in fact is capable of protecting itself in this way, and the system of plant auto detoxification involving biological molecules has been reviewed by PRASAD (1998). An example of this phenomenon is the complexation of lead by the polysaccharide, rhamnogalacturonane II (PELLERIN, 1997). Furthermore, since there is a limited amount of industrial activities and automobile traffic in the Azores by comparison with the continent, the degree of atmospheric lead pollution is lower as are thus the concentrations found in the grapes of these islands.

The levels of lead in wines differ from one region to the next reflecting the varying soil concentrations of this element. The wines of Pico have a mean lead concentration of 18.5 µg/l; the individual mean concentrations in white and red wines were respectively 20.4 µg/l and 16.1 µg/l. The white wines of Biscoitos were found to contain 40.1 µg/l and those of Graciosa, 31.8 µg/l. For cadmium, however, there are also major differences in the concentrations found among the three regions. The mean cadmium concentration of all Pico wines was 0.14 µg/l (0.2 µg/l and 0.04 µg/l for white and red wines, respectively). In Biscoitos the mean cadmium concentration in white wines is 0.35 µg/l and in Graciosa, 1.31 µg/l. The soils analysed in this study, in particular Graciosa, presented levels of cadmium greater than the recommended values which translates into higher cadmium wine concentrations in this region. However, it should be noted that for both elements, the levels found are significantly lower than the limits imposed by the OIV, i.e. 200 µg/l for lead and 10 µg/l for cadmium. It is important to take into account the influence of the type of vinification used, as in general white wines have a greater mineral content than red wines. Indeed, this emphasises the importance of maceration in the elimination of toxic elements contained in the grapes (must) and also the role played by macromolecules, for example rhamnogalacturonan- type polysaccharides in metal complexation. In this study, the average wine concentrations were 28.3 µg/l and 0.58 µg/l for lead and cadmium, res-

pectively. Comparison of these figures with those reported by CABANIS *et al.* (1998) (60 µg/l and 1.1 µg/l for lead and cadmium, respectively) or with those reported by HERNANDEZ (1994) who found a mean concentration of 289 µg/l of lead in 75 wines of the Canary Islands, would indicate that the levels of toxic metals are significantly lower in the Azores.

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