

Influence of Different Mineral and Organic Pesticide Treatments on Cd(II), Cu(II), Pb(II), and Zn(II) Contents Determined by Derivative Potentiometric Stripping Analysis in Italian White and Red Wines

FRANCESCO SALVO,[†] LARA LA PERA,[†] GIUSEPPA DI BELLA,[†]
MARIANO NICOTINA,[‡] AND GIACOMO DUGO^{*,†}

Dipartimento di Chimica Organica e Biologica, University of Messina, Salita Sperone 31, 98166 Messina, Italy, and Dipartimento di Entomologia e Zoologia Agraria, University of Napoli, Via Università 100, 80055 Napoli, Italy

This paper deals with the use of derivative potentiometric stripping analysis (dPSA) as a rapid and precise method to determine Cd(II), Cu(II), Pb(II), and Zn(II) levels in red and white wine samples from Sicily, Campania, and Tuscany and to investigate the possible connection between the content of these metals and the pesticide treatments used in vine-growing to control plant diseases and pests. dPSA allowed direct quantitation of heavy metals in acidified wines without any sample pretreatment. Mean recoveries of Cd(II), Cu(II), Pb(II), and Zn(II) ranged from 95.5 to 99.2% for white wine samples and from 96.1 to 100.0% for red wine samples. The obtained results showed that Cd(II) was not found in any sample and that Cu(II), Pb(II), and Zn(II) levels were always lower than the toxicity limits in both fungicide- and water-treated wines. Nevertheless, the contents of metals were increased in samples from organic and inorganic pesticides treatment with respect to the water-treated samples. In particular, quinoxifen, dinocap-penconazole, and dinocap applications considerably increased Cu(II) and Zn(II) contents in white and red wines. The levels of lead were significantly raised by azoxystrobin and sulfur treatments.

KEYWORDS: Derivative potentiometric stripping analysis; heavy metals; pesticides; wines

INTRODUCTION

Wine is a widely consumed beverage with thousands of years of tradition, so an accurate quantitative knowledge of the presence of toxic elements such as heavy metals, and their possible source of contamination, is very important from both toxicological and enological points of view. The trace elements composition of wines results from many factors such as the type of soil, wine-processing equipment, vinification methods (1), and agrochemical treatments (2). Viticulture is closely associated with the use of pesticides (3), so the purpose of this work is to investigate the possible correlation between the presence of Cd(II), Cu(II), Pb(II), and Zn(II) in samples of Italian white and red wines and the pesticide treatments used in vine-growing. Derivative potentiometric stripping analysis (dPSA) was used to determine the concentrations of these metals in wine. dPSA is a rapid, sensitive, and accurate method for trace and ultratrace metal quantitation in food matrices. By the use of dPSA, La Pera et al. have already studied the connection between the presence of lead in olive oils and organophosphate pesticide treatments applied on olive trees (4). Many publications are

available concerning the analytical determination of pesticide residues (5–7) and their metabolites and heavy metals (8–11) in wine. Meanwhile, there is a lack of data regarding the relationship between the concentration of heavy metals in wine and the use of pesticides (12–14). Attention is focused on these four metals because Cu(II) and Zn(II), at low concentrations, are important in the fermentative process (15), whereas at high concentration they negatively influence the quality of wines (16, 17), particularly its organoleptic properties (18). On the other hand, Cd(II) and Pb(II) are known to be potentially toxic (19); their presence in wine originates mostly from environmental and technological contamination.

Maximum acceptable levels of Cd(II), Cu(II), Pb(II), and Zn(II) in wines have been established by the Italian Republic (20) and by the European Commission (21), respectively, at 0.1, 1.0, 0.3, and 0.5 mg L⁻¹. The analytical techniques conventionally used for metals determinations are both emission and absorption spectrophotometric (22) as well as electroanalytical techniques (8). These analytical methods require sample pretreatments suitable for the complete destruction of the organic matrix such as wet digestion, dry ashing, and microwave oven dissolution (23, 24). dPSA allows the direct determination of heavy metals in wines without any sample pretreatment except acid adjust-

[†] University of Messina.

[‡] University of Napoli.

ment, because the glassy carbon mercury film working electrode (GCMFE) remains inert to organic molecule interferences during the signal collection phase (25).

EXPERIMENTAL PROCEDURES

Apparatus. Metals analysis was carried out by a PSA ION 3 potentiometric stripping analyzer (Steroglass, S. Martino in Campo, Perugia, Italy) (26, 27), connected to an IBM-compatible personal computer. The analyzer operated under the control of the NEOTES 2.0.1 software package (Steroglass). The analytical procedure can be completely controlled by this program. The analyzer was equipped with a conventional three-electrode cell. The working electrode was a glassy carbon one coated with a thin mercury film; the reference electrode was an Ag/AgCl electrode (3 M KCl), and a platinum wire auxiliary electrode was used. A pH-meter MI229 BDH equipped with glass plus combination pH electrodes (BDH, Milan, Italy) was used to measure the pH values of the wine samples. To confirm the results of the potentiometric method, wine samples were subjected to atomic absorption spectrometric analysis, using a Shimadzu 800 series graphite furnace atomic absorption spectrometer, equipped with autosampler ASC-6100.

Reagents. All glassware was rinsed with 10% (v/v) nitric acid. Ultrapure water ($18.2 \text{ Mohm cm}^{-1}$) was obtained from a Pure Lab RO and a Pure Lab UV system (USF, Ransbach-Baumbach, Germany). Ultrapure hydrochloric acid (34–37%), Hg(II) ($1000 \mu\text{g mL}^{-1}$, 1 M in hydrochloric acid), and Cd(II), Cu(II), Pb(II), Zn(II), Ga(III), and Pd(II) ($1000 \mu\text{g mL}^{-1}$, 0.5 N in nitric acid) standard solutions were purchased by Panreac Quimica (Barcelona, Spain). By dilution with ultrapure water, a solution containing 2 N HCl, $1.0 \mu\text{g mL}^{-1}$ solutions of Cd(II), Cu(II), Pb(II), and Zn(II), a $10 \mu\text{g mL}^{-1}$ solution of Ga(III), and a $100 \mu\text{g mL}^{-1}$ solution of Pd(II) were prepared.

Wines Characteristics and Pesticide Treatments. All wines were sampled in dark glass bottles with corks and stored at $4 \text{ }^\circ\text{C}$ for the duration of the experimentation.

The white wines, vinified in the crop year 2000, came from Sicily and Campania. Particularly, Sicilian wines were produced from plants 15–20 years old, grown on Etna (300 m elevation) (S. Venerina, Catania, Italy), in a volcanic soil. The vines were grafted with Inzolia and Carricante variety in ratio 1:1. The wines from Campania were produced from plants 25 years old, grown on Montefredane hills (700 m elevation) (Avellino, Italy), in a clayey soil. The vines were grafted with Fiano d'Avellino variety. Red wines from Tuscany were produced in the crop year 2000, from plants 25 years old, cultivated along the Maremma Toscana coast (100 m elevation) (Grosseto, Italy), on a calcareous soil. The vines were grafted with Sangiovese variety, Morellino clone.

White Vinification. Newly cropped *Vitis vinifera* fruits from Sicily and Campania were crushed and destemmed and then subjected to soft pressing by a pneumatic press. The obtained must was treated with SO_2 (30 g/hL), pectolytic enzymes (1.5 g/hL), and vitamin C (5 g/hL) to favor clarification before fermentation; the temperature was maintained at $8 \text{ }^\circ\text{C}$ for 24 h. The must was spiked with 20 g/hL of thiamin and ammonium phosphate as fermentation coadjuvants, and then it was inoculated with 30 g/hL of selected *Saccharomyces cerevisiae* yeasts. Fermentation was performed at $15 \text{ }^\circ\text{C}$. To remove lees, after fermentation, the wine was decanted into a tank and spiked with SO_2 (5 g/hL). After 10 days, the wine was decanted again and treated with SO_2 (5 g/hL). Subsequently, the wine was twice filtered through 1 and $0.45 \mu\text{m}$ cardboard filters, spiked with SO_2 (2–3 g/hL), and bottled in dark bottles at $4 \text{ }^\circ\text{C}$ for the duration of the experimentation. Each sample was separately vinified, following the protocol mentioned above.

Red Vinification. Newly cropped *V. vinifera* fruits from Tuscany were crushed and destemmed and then spiked with SO_2 (5 g/hL), selected yeasts (30 g/hL) and allowed to ferment for 10 days at $28 \text{ }^\circ\text{C}$, effecting three fullings a day. The wine was drawn from the vat, and the vinasses were crushed by a hydraulic press. After 4 weeks, the lees were removed and the wine was spiked with SO_2 (2–3 g/hL). Subsequently, the wine was spiked again with SO_2 (2–3 g/hL) and bottled in dark bottles at $4 \text{ }^\circ\text{C}$ for the duration of the experimentation. Each sample was separately vinified, following the protocol mentioned above.

Table 1. Cd, Cu, Pb, and Zn Concentrations in Eight Samples of White Wines from Sicily^a

sample	treatment	ng mL ⁻¹			
		Cd	Cu	Pb	Zn
blank	water	nd ^b	20.6 ± 0.7	9.0 ± 0.9	21.6 ± 1.1
Organic Treatments					
1	quinoxifen	nd	63.3 ± 1.8	10.3 ± 1.1	23.7 ± 0.8
2	fenarimol	nd	27.8 ± 1	11.4 ± 0.9	53.1 ± 0.3
3	azoxystrobin	nd	26.8 ± 0.8	16.7 ± 1.4	52.6 ± 1.3
4	dinocap-penconazole	nd	23.2 ± 0.7	9.6 ± 0.8	26.7 ± 0.6
5	dinocap	nd	24.4 ± 1.2	13.0 ± 1.3	21.6 ± 1.0
mean \pm SD			33.1 ± 17.0	12.2 ± 2.8	35.5 ± 15.9
Inorganic Treatments					
6	S WP ^c	nd	36.1 ± 1.2	13.8 ± 1.0	47.2 ± 1.6
7	S DP ^d	nd	29.4 ± 1.3	26.0 ± 1.3	53.7 ± 2.0
mean \pm SD			32.8 ± 4.7	19.9 ± 8.6	50.5 ± 4.6
total mean \pm SD			31.5 ± 13.7	13.7 ± 5.6	37.4 ± 15.3

^a One was treated with water only (blank), the others were subjected to different organic and inorganic pesticide treatments. Each value is the mean of three determinations. ^b nd, not detectable ($<1.5 \text{ ng mL}^{-1}$). ^c S WP, sulfur wettable powder. ^d S DP, sulfur dry powder.

Table 2. Cd, Cu, Pb, and Zn Concentrations in Eight Samples of White Wines from Campania^a

sample	treatment	ng mL ⁻¹			
		Cd	Cu	Pb	Zn
blank	water	nd ^b	31.0 ± 0.8	3.6 ± 0.3	77.6 ± 2.0
Organic Treatments					
1	quinoxifen	nd	185.3 ± 5.9	4.2 ± 0.2	111.9 ± 1.7
2	fenarimol	nd	184.2 ± 2.7	5.1 ± 0.3	205.5 ± 4.3
3	azoxystrobin	nd	203.0 ± 1.9	13.1 ± 1.2	200.8 ± 4.7
4	dinocap-penconazole	nd	247.1 ± 6.5	4.7 ± 0.8	109.1 ± 3.0
5	dinocap	nd	72.4 ± 1.0	4.1 ± 0.4	142.1 ± 2.6
mean \pm SD			178.8 ± 64.5	6.2 ± 2.9	133.9 ± 79.3
Inorganic Treatments					
6	S WP ^c	nd	110.8 ± 4.0	12.6 ± 0.2	178.8 ± 2.5
7	S DP ^d	nd	174.6 ± 4.0	15.4 ± 0.8	176.6 ± 2.9
mean \pm SD			142.7 ± 45.1	14.0 ± 2.0	177.7 ± 1.6
total mean \pm SD			151.1 ± 72.7	7.8 ± 4.9	150.3 ± 47.2

^a One was treated with water only (blank); the others were subjected to different organic and inorganic pesticide treatments. Each value is the mean of three determinations. ^b nd, not detectable ($<1.5 \text{ ng mL}^{-1}$). ^c S WP, sulfur wettable powder. ^d S DP, sulfur dry powder.

Pesticides Treatments. Pesticides were used at the doses recommended by the manufacturer and were sprayed with a manual sprayer in the three Italian vineyards. As **Tables 1–3** report, samples 1–5 of each group of wines were respectively treated with quinoxifen, fenarimol, azoxystrobin, dinocap-penconazole, and dinocap; samples 6 and 7 were treated with dry sulfur powder and wettable sulfur powder, respectively. To compare with treated samples, one sample, the “blank”, was treated with water only. In Sicily and Campania, each fungicide treatment was applied every 15 days during the vine maturation phase and repeated six times in this period. In Tuscany, each fungicide treatment was applied every 12 days during the vine maturation phase and repeated nine times in this period.

Procedure. Sample Treatments. dPSA allowed the direct determination of Cd(II), Cu(II), Pb(II), and Zn(II) in acidified wine samples. Before each analysis, an appropriate volume of wine was treated with 2 M HCl, lowering the pH to 2, to ensure that all metals present remained in unbound free forms and insoluble oxide formation was prevented. The acidification was carried out by adding HCl with a Pasteur pipet, keeping the wine sample under magnetic stirring and continuously measuring the pH value by the glass electrode. After

Table 3. Cd, Cu, Pb, and Zn Concentrations in Eight Samples of Red Wines from Tuscany^a

sample	treatment	ng mL ⁻¹			
		Cd	Cu	Pb	Zn
blank	water	nd ^b	10.5 ± 0.5	5.0 ± 0.4	105.0 ± 2.9
Organic Treatments					
1	quinoxifen	nd	415.7 ± 12.5	12.6 ± 0.9	263.0 ± 8.0
2	fenarimol	nd	103.3 ± 2.3	14.4 ± 1.0	166.7 ± 6.3
3	azoxystrobin	nd	397.0 ± 14.9	17.4 ± 1.1	103.3 ± 5.2
4	dinocap-penconazole	nd	253.9 ± 10.0	9.0 ± 0.8	179.3 ± 7.0
5	dinocap	nd	325.2 ± 7.3	9.5 ± 0.7	152.2 ± 5.4
mean ± SD			304.4 ± 128.7	12.6 ± 3.5	172.9 ± 58.0
Inorganic Treatments					
6	S WP ^c	nd	20.1 ± 2.3	17.2 ± 0.2	266.9 ± 9.1
7	S DP ^d	nd	61.4 ± 3.3	16.6 ± 1.0	257.8 ± 8.9
mean ± SD			40.8 ± 28.2	16.9 ± 0.5	262.4 ± 6.4
total mean ± SD			198.4 ± 169.3	12.7 ± 4.5	186.8 ± 68.2

^a One was treated with water only (blank); the others were subjected to different organic and inorganic pesticide treatments. Each value is the mean of three determinations. ^b nd, not detectable (<1.5 ng mL⁻¹). ^c S WP, sulfur wettable powder. ^d S DP, sulfur dry powder.

Table 4. Repeatability Tests for White and Red Wines, Obtained by Eight Determinations

	Cd	Cu	Pb	Zn
(A) White Wines				
mean ± SD (ng mL ⁻¹)	19.6 ± 0.5	64.6 ± 1.4	4.2 ± 0.1	58.6 ± 1.7
repeatability %	97.4	97.8	96.9	97.1
(B) Red Wines				
mean ± SD (ng mL ⁻¹)	19.8 ± 0.7	203.0 ± 1.9	12.4 ± 0.3	53.1 ± 1.3
repeatability %	95.6	99.1	97.2	97.6

acidification, the sample was left under magnetic stirring for 30 min to ensure a complete dissociation of metal complex, and then the dilution ratio was calculated.

Potentiometric Determination. The electrodes were stored in ultrapure water. Before the start of each analysis, they were well cleaned with pure absolute methanol and filter paper. The plating of the working electrode was executed as reported in a previous paper (26). Cd(II), Cu(II), and Pb(II) were determined simultaneously by putting into the electrochemical cell 7.0 mL of acidified wine together with 13.0 mL of ultrapure water and a 1.0 mL volume of 1000 µg mL⁻¹ Hg(II) standard solution as oxidant agent. Zn(II) analysis was separately executed (26) by putting into the cell 3.0 mL of acidified wine, 17.0 mL of ultrapure water, 0.5 mL of 1000 µg mL⁻¹ Hg(II), and 0.2 mL of 10 µg mL⁻¹ Ga(III) solution to prevent Cu–Zn intermetallic compound formation on the mercury film (26, 28). All potentiometric conditions are reported in previous papers (26, 27). Quantitative analysis was executed by the multiple-point standard additions method (29): optimum precision and accuracy were obtained by executing two additions of each metal's 1.0 µg mL⁻¹ standard solution and performing the measurements four times. Calibration curves with correlation coefficients >99.5% were obtained.

Repeatability. The repeatability of the method was evaluated by carrying out the determinations eight times on a sample of white wine and a sample of red wine (Table 4), acidified as already described. The values obtained were subjected to statistical analysis by employing the same software as that used for the analytical steps. Cadmium(II) was not found in any sample, so the repeatability was evaluated by spiking two samples each of white and red wines with an appropriate quantity of Cd(II) and repeating the analysis eight times.

Recovery Tests. The recovery tests were separately executed on red and white wines by spiking the samples at different levels with appropriate volumes of each metal standard solution (1.0 µg mL⁻¹). Both spiked and unspiked samples were analyzed three times according

to the proposed method. The obtained recoveries for the white wine sample were 95.5 ± 1.2% for Cd(II), 99.2 ± 2.4% for Cu(II), 98.8 ± 1.9% for Pb(II), and 98.3 ± 1.9% for Zn(II). The obtained recoveries for the red wine sample were 96.1 ± 1.2% for Cd(II), 97.1 ± 1.6% for Cu(II), 100.0 ± 2.1% for Pb(II), and 99.5 ± 2.7% for Zn(II).

Detection Limits. The theoretical instrumental detection limits were calculated by utilizing the expression $3\sigma/S$ (30), as reported in a previous paper (26). The values estimated for the white wine were 1.5, 1.8, 1.0, and 2.0 ng mL⁻¹, respectively, for Cd(II), Cu(II), Pb(II), and Zn(II). The detection limits for the red wine were 1.4, 1.7, 1.1, and 1.7 ng mL⁻¹, respectively, for Cd(II), Cu(II), Pb(II), and Zn(II).

GF-AAS Confirmation Analysis. The AAS analysis was executed on two samples of white wines and on two red ones. Before the spectroscopic analysis, the samples were acidified as already described. Each analysis requested 0.25 mL of sample. The determination of cadmium and lead was carried out by adding, for each injection, 5 µL of a PdNO₃ solution (Pd concentration = 100 µg mL⁻¹), as matrix modifier. The working wavelengths were 228.8 nm for Cd, 324.8 nm for Cu, 283.3 nm for Pb, and 213.9 nm for Zn. Obtained results are listed in Table 5.

RESULTS AND DISCUSSION

The presence of Cd(II), Cu(II), Pb(II), and Zn(II) was evaluated by dPSA in eight samples of white wine produced in Sicily (Table 1), in eight samples of white wine produced in Campania (Table 2), and in eight samples of red wine produced in Tuscany (Table 3). The samples were grouped according to their place of origin. Therefore, each group was composed by wine samples originating from the same vineyard and subjected to the same agronomic and climatic conditions and vinification and storage processes. Among the wines belonging to the same group, the only difference was the pesticide treatments, which in the present work were considered to be the one variable that may influence the concentration of Cd(II), Cu(II), Pb(II), and Zn(II). Five organic fungicide treatments—quinoxifen, fenarimol, azoxystrobin, dinocap-penconazole, and dinocap—and two inorganic treatments—sulfur wettable powder (WP) and sulfur dry powder (DP)—were employed in the experimentation. The heavy metals content of samples treated with the fungicides was compared with that found in the water-treated sample. Cd(II) was not found in any sample, and Cu(II), Pb(II), and Zn(II) levels were always lower than the toxicity limits both in fungicide-treated wines and in water-treated wines.

White Wines from Sicily. The blank showed the lowest levels of Cu(II), Pb(II), and Zn(II).

The content of copper was significantly higher with respect to the blank (20.6 ± 0.7 ng mL⁻¹) in sample 1 (63.3 ± 1.8 ng mL⁻¹), from the quinoxifen treatment, and in sample 6 (36.1 ± 1.2 ng mL⁻¹) from the sulfur WP treatment. Samples 2–5 and 7, respectively from fenarimol, azoxystrobin, dinocap-penconazole, dinocap, and sulfur DP treatments, presented Cu(II) levels in the range of 23–30 ng mL⁻¹.

The content of lead was considerably higher compared with the blank (9.0 ± 0.9 ng mL⁻¹) in most wines of the group. It ranged from 13 to 17 ng mL⁻¹ in samples 3, 5, and 6 treated with azoxystrobin, dinocap, and sulfur WP, respectively. Sample 7 (26.0 ± 1.2 ng mL⁻¹), treated with sulfur DP, presented the highest lead content, which was tripled with respect to the blank. Meanwhile, samples 1, 2, and 4 from quinoxifen, fenarimol, and dinocap-penconazole treatments, showed Pb(II) levels similar to that found in the blank.

The content of zinc was significantly higher compared with the blank (21.6 ± 1.1 ng mL⁻¹) in most wines of the group. It spanned from 47–54 ng mL⁻¹ in samples 2, 3, 6, and 7, respectively from fenarimol, azoxystrobin, sulfur WP, and sulfur DP treatments. The zinc contents of samples 1 and 5, respec-

Table 5. Metals Concentrations and Standard Deviations, Determined by dPSA and GFAAS^a

sample	ng mL ⁻¹							
	Cd		Cu		Pb		Zn	
	dPSA	GFAAS	dPSA	GFAAS	dPSA	GFAAS	dPSA	GFAAS
white 1	nd ^b	nd	184.2 ± 2.7	181.9 ± 3.6	5.1 ± 0.3	4.7 ± 0.4	205.5 ± 4.3	207.7 ± 3.7
white 2	nd	nd	63.3 ± 1.8	62.9 ± 2.2	10.3 ± 1.1	9.9 ± 1.9	23.7 ± 0.8	22.6 ± 0.6
red 1	nd	nd	103.3 ± 2.3	102.9 ± 2.1	14.4 ± 1.0	13.3 ± 1.5	166.7 ± 6.3	165.1 ± 5.0
red 2	nd	nd	325.2 ± 7.3	319.1 ± 6.5	9.5 ± 0.7	8.8 ± 0.9	152.2 ± 5.4	147.8 ± 6.3

^a Each value is the mean of five determinations. ^b nd, not detectable.

tively treated with quinoxifen and dinocap, were almost identical to that found in the blank.

White Wines from Campania. The blank showed the lowest levels of Cu(II), Pb(II), and Zn (II).

The content of copper was remarkably higher with respect to the blank ($31.0 \pm 0.8 \text{ ng mL}^{-1}$) for all of the samples. Particularly, it was included in the range $170\text{--}250 \text{ ng mL}^{-1}$ for samples 1–4 and 7, respectively treated with quinoxifen, fenarimol, azoxystrobin, dinocap-penconazole, and sulfur DP. Samples 5 ($72.4 \pm 1.0 \text{ ng mL}^{-1}$) and 6 ($110.8 \pm 1.0 \text{ ng mL}^{-1}$), from dinocap and sulfur WP treatments, respectively, presented lower concentrations; however, they were higher than the blank.

The content of lead found in samples 3, 6, and 7 from azoxystrobin, sulfur WP, and sulfur DP treatments, respectively, was included in the range $12.0\text{--}15.5 \text{ ng mL}^{-1}$; it was significantly higher than that estimated for the blank ($3.6 \pm 0.3 \text{ ng mL}^{-1}$). Samples 1, 2, 4, and 5, respectively from quinoxifen, fenarimol, dinocap-penconazole, and dinocap treatments, had Pb(II) levels close to that found in the blank.

The content of zinc was significantly higher with respect to the blank ($77.6 \pm 2.0 \text{ ng mL}^{-1}$) for all of the samples; particularly, it was included in the range $170.0\text{--}210.0 \text{ ng mL}^{-1}$ for samples 2, 3, 6, and 7 from fenarimol, azoxystrobin, sulfur WP, and sulfur DP treatments, respectively. Meanwhile, samples 1, 4, and 5, treated with quinoxifen, dinocap-penconazole, and dinocap, respectively, presented lower Zn(II) concentrations that spanned from 110.0 to 143.0 ng mL^{-1} .

Red Wines from Tuscany. The blank showed the lowest levels of Cu(II) and Pb(II). Samples 1 and 3–5, respectively from quinoxifen, azoxystrobin, dinocap-penconazole, and dinocap treatments, presented copper levels included in the range $250\text{--}420 \text{ ng mL}^{-1}$. These values were enormously higher in comparison with the blank copper concentration ($10.5 \pm 0.5 \text{ ng mL}^{-1}$). Samples 6 ($20.1 \pm 2.3 \text{ ng mL}^{-1}$) and 7 ($61.4 \pm 3.3 \text{ ng mL}^{-1}$), respectively from sulfur WP and sulfur DP treatments, had reduced contents of the metal, but they were higher than that of the blank.

The lead content of all the samples was significantly higher than that found in the blank ($5.0 \pm 0.4 \text{ ng mL}^{-1}$). Particularly samples 1–3, 6, and 7, respectively from quinoxifen, fenarimol, azoxystrobin, sulfur WP, and sulfur DP treatments, showed lead levels that spanned from 12.5 to 17.5 ng mL^{-1} . Almost identical lead levels, doubled with respect to the blank value, were found in samples 4 and 5 ($\sim 9.0 \text{ ng mL}^{-1}$), from dinocap-penconazole and dinocap treatments, respectively.

The lowest content of zinc was found in sample 3 from the azoxystrobin treatment ($103.3 \pm 5.2 \text{ ng mL}^{-1}$), which considering the standard deviation (SD) range, was almost identical to that found in the blank, $105.5 \pm 2.9 \text{ ng mL}^{-1}$. All of the other wines of this group had a remarkably higher content of Zn(II) in comparison with the blank. Particularly, samples 1, 6, and 7 from quinoxifen, sulfur WP, and sulfur DP treatments, respectively, had almost the same Zn (II) levels ($\sim 260.0 \text{ ng mL}^{-1}$).

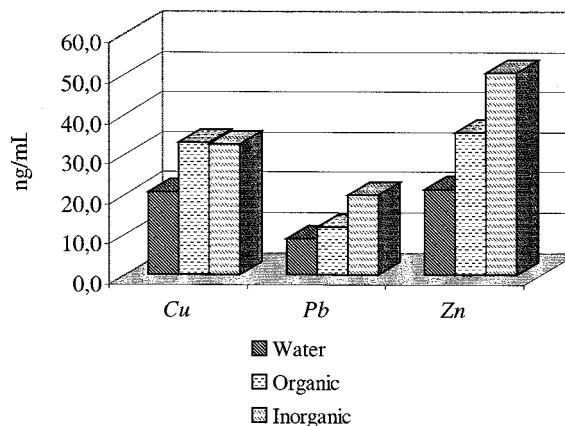


Figure 1. Influence of organic (mean metals content of quinoxifen-, fenarimol-, azoxystrobin-, dinocap-penconazole-, and dinocap-treated samples) and inorganic (mean metals content of sulfur WP- and sulfur DP-treated samples) treatments over the content of Cu, Pb, and Zn, with respect to the water-treated sample, in Sicilian wines.

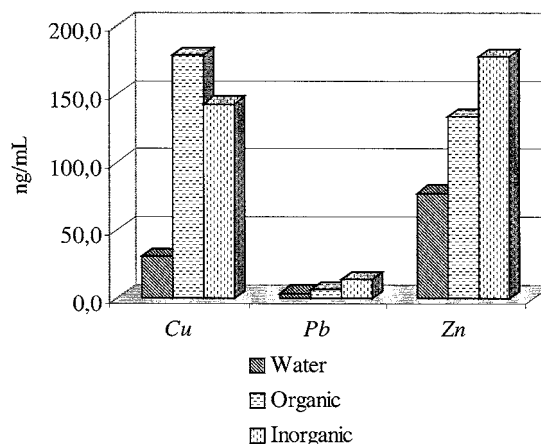


Figure 2. Influence of organic (mean metals content of quinoxifen-, fenarimol-, azoxystrobin-, dinocap-penconazole-, and dinocap-treated samples) and inorganic (mean metals content of sulfur WP- and sulfur DP-treated samples) treatments over the content of Cu, Pb, and Zn, with respect to the water-treated sample, in wines from Campania.

Samples 2, 4, and 5 from fenarimol, dinocap-penconazole, and dinocap treatments, respectively, had zinc contents that ranged from 150.0 to 180.0 ng mL^{-1} .

Figures 1–3 show that the influences of organic (quinoxifen, fenarimol, azoxystrobin, dinocap-penconazole, and dinocap) and inorganic (sulfur WP and sulfur DP) treatments on Cu(II), Pb(II),

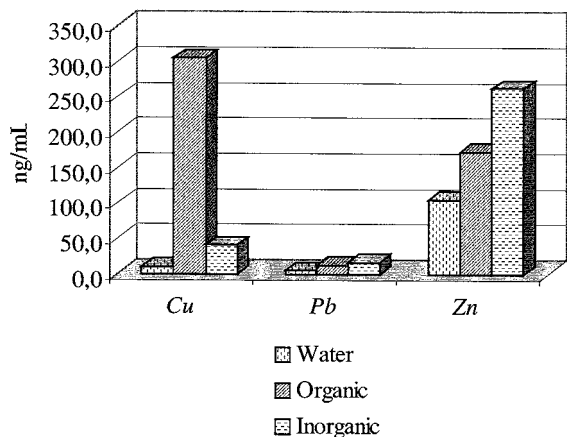


Figure 3. Influence of organic (mean metals content of quinoxifen-, fenarimol-, azoxystrobin-, dinocap-penconazole-, and dinocap-treated samples) and inorganic (mean metals content of sulfur WP- and sulfur DP-treated samples) treatments over the content of Cu, Pb, and Zn, with respect to the water-treated sample, in wines from Tuscany.

and Zn(II) levels in wines from Sicily, Campania, and Tuscany, with respect to the water-treated samples of each group, are similar. Particularly, in almost all of the treated samples from Campania and Tuscany, the copper and zinc contents were remarkably higher than the blank; this influence is particularly evident for quinoxifen-, dinocap-penconazole-, and dinocap-treated wines. Moreover, it was evident for the three groups that the influence of sulfur WP, sulfur DP, and azoxystrobin treatments on lead content was appreciably increased with respect to the blank.

LITERATURE CITED

- Golimowsky, J.; Valenta, P.; Wolfgang-Nurnberg, H. Toxic trace metals in food II. A comparative study of the levels of toxic trace metals in wine by differential pulse anodic stripping voltammetry and electrothermal atomic absorption spectrometry. *Z. Lebensm. Unters. Forsch.* **1979**, *168*, 439–443.
- Hsia, C.; Planck, R. W.; Nagel, C. W. Influence of must processing on iron and copper contents of experimental wines. *Am. J. Enol. Vitic.* **1975**, *26*, 57–61.
- Fernandez-Cornejo, J. Environmental and economic consequences of technology adoption: IPM in viticulture. *Agric. Econ.* **1998**, *18*, 145–155.
- La Pera, L.; Lo Curto, S.; Dugo, G.; Lo Coco, F.; Liberatori, A. Determination of copper(II), lead(II), cadmium(II) and zinc(II) in olive oils from Sicily and Puglia by derivative potentiometric stripping. Presented at the European Conference on Advanced Technology for Safe and High Quality Foods, Berlin, Germany, Dec 5–7, 2001.
- Rial Otero, R.; Yagui Ruitz, C.; Cancho Grande, B.; Simal Gándara, J. Solid phase microextraction chromatographic mass spectrometric method for the determination of fungicides cipro-dynil and fludioxonil in white wines. *J. Chromatogr. A* **2002**, *4*, 41–52.
- Cabras, P.; Angioni, A.; Garau, V. L.; Pirisi, F. M.; Cabizza, F.; Farris, G. A. Fate of quinoxifen residues in grapes, wines and their processing products. *J. Agric. Food Chem.* **2000**, *48*, 6128–6131.
- Dugo, G.; Visco, A.; Saitta, M.; Vinci, V.; Di Bella, G. Dosaggio di quinoxifen su prodotti vitivinicoli Siciliani. *Vignevini* **2001**, *7/8*, 93–95.
- Balduini, P. L.; Cavalli, S.; Lal Sharma, J. Determination of transition metals in wine by IC, DPASV-DPCSV and ZGFAAS

- coupled with UV photolysis. *J. Agric. Food Chem.* **1999**, *47*, 1993–1998.
- Baxter, M. J.; Crews, H. M.; Dennis, J.; Goodall, I.; Anderson, D. The determination of the authenticity of wine from its trace metals composition. *Food Chem.* **1997**, *60*, 443–450.
- Murány, Z.; Kovács, Z. Statistical evaluation of aroma and metal content in Tokay wines. *Microchem. J.* **1999**, *67*, 91–96.
- Megna, C.; Cabrera, C.; Lorenzo, M. L.; Lòpez, M. C. Cadmium levels in wine beer and other alcoholic beverages: possible source of contamination. *Sci. Total Environ.* **1996**, *181*, 201–208.
- Eschnauer, H.; Neeb, R. Micro-elements analysis in wine and grapes. In *Modern Methods for Plants Analysis*; Linskens, H. I., Jackson, J. F., Eds.; Springer-Verlag: Berlin, Germany, 1988; pp 67–91.
- Al Nasir, F. M.; Jiries, A. G.; Batarseh, M. I.; Beese, F. Pesticides and trace metals residue in grape and home-made wine in Jordan. *Environ. Monit. Assessment* **2001**, *66*, 253–263.
- Maheffy, K. R.; Corneliussen, P. E.; Jelinek, C. F.; Fiorino, J. A. Heavy metals exposure from food. *Environ. Health Perspect.* **1975**, *12*, 63–69.
- Ribéreau-Gayon, J.; Peynaud, E.; Ribéreau-Gayon, P. Precipitation dans le Vins. In *Sciences et Techniques du Vin*, 2nd ed.; Bordas: Paris, France, 1976; Vol. 3, pp 567–616.
- Fernandez Pereira, C. The importance of metallic elements in wine. A literature survey. *Z. Lebensm. Unters. Forsch.* **1998**, *186*, 295–300.
- McKinnon, A. J.; Scollary, G. R. Size fractionation of metals in wine using ultrafiltration. *Talanta* **1997**, *44*, 1649–1658.
- Gennaro, M. C.; Mentasti, E.; Sarzanini, C.; Pesticcio, A. Undesirable and harmful metals in wines—determination and removal. *Food Chem.* **1986**, *19*, 93–104.
- Scollary, G. R. Metals in wine: contamination, spoilage and toxicity. *Analysis* **1997**, *25*, 26–30.
- Repubblica Italiana. Caratteristiche e Limiti di alcune Sostanze nel Vino, Dec 1986, D.M. 29.
- European Commission. 1997, Doc III/5125/95/Rev. 3.
- European Economic Community. *Official Methods of Analysis of Wine*; 1990.
- Reid, H. J.; Greenfield, S.; Edmonds, T. E. Investigation of decomposition products of microwave digestion of food sample. *Analyst (London)* **1995**, *120*, 1543–1548.
- Allen, S. E.; Grimshaw, H. M.; Parkinson, J. A.; Quarambay, C. *Chemical Analysis of Ecological Material*; Blackwell: Oxford, U.K., 1989; pp 84–88.
- Sahlin, E.; Jagner, D.; Ratana-Ohpas, R. Mercury nucleation on glassy carbon electrode. *Anal. Chim. Acta* **1997**, *346*, 157–164.
- La Pera, L.; Lo Curto, S.; Visco, A.; La Torre, L.; Dugo, G. Derivative potentiometric stripping analysis (dPSA) used for determination of cadmium, copper, lead, and zinc in Sicilian olive oils. *J. Agric. Food Chem.* **2002**, *50*, 3090–3093.
- La Pera, L.; Lo Coco, F.; Mavrogeni, E.; Giuffrida, D.; Dugo, G. Determination of copper(II), lead(II), cadmium(II) and zinc(II) in virgin olive oils produced in Sicily and Apulia by derivative potentiometric stripping analysis. *Ital. J. Food Sci.* **2002**, in press.
- Jagner, D. Instrumental approach to potentiometric stripping analysis of some heavy metals. *Anal. Chim.* **1978**, *50*, 1924–1929.
- Renman, R.; Jagner, D. Asymmetric distribution of results in calibration curve and standard addition evaluation. *Anal. Chim. Acta* **1997**, *357*, 157–166.
- Ensafi, A. A.; Zarei, K. Simultaneous determination of trace amounts of cadmium, nickel and cobalt in water samples by adsorptive voltammetry using ammonium 2-amino-cyclopentene dithiocarboxylate as a chelating agent. *Talanta* **2000**, *52*, 435–440.

Received for review July 7, 2002. Revised manuscript received October 11, 2002. Accepted October 14, 2002.

JF020818Z