Heavy metal pollution in soil: a survey on west-central Sardinian long-term vineyards (Italy)

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Many agricultural practices can affect fertility, and suitability of agricultural soils. The sustainability of a soil agroecosystem can be strongly affected by the presence of heavy metals (Knox *et al.* 1999; Giller *et al.* 1997). Copper is used since 1883 in agricultural activities thanks to its action against downy mildew (*Plasmopara viticola*) on vineyards. Nowadays, its uses is widespread as copper sulfate (Bordeaux mixture) or combined with systemic fungicides. The long-term vineyards have received strong intakes of copper that can lead to accumulation in soils with possible repercussions on the soil suitability. Moreover, its concentration can be related with the age of the vineyards (Fregoni *et al*. 1984; Leonardi *et al*. 2002).

Fig.1.The Sardinia Region, the area under study, and the sampling points.

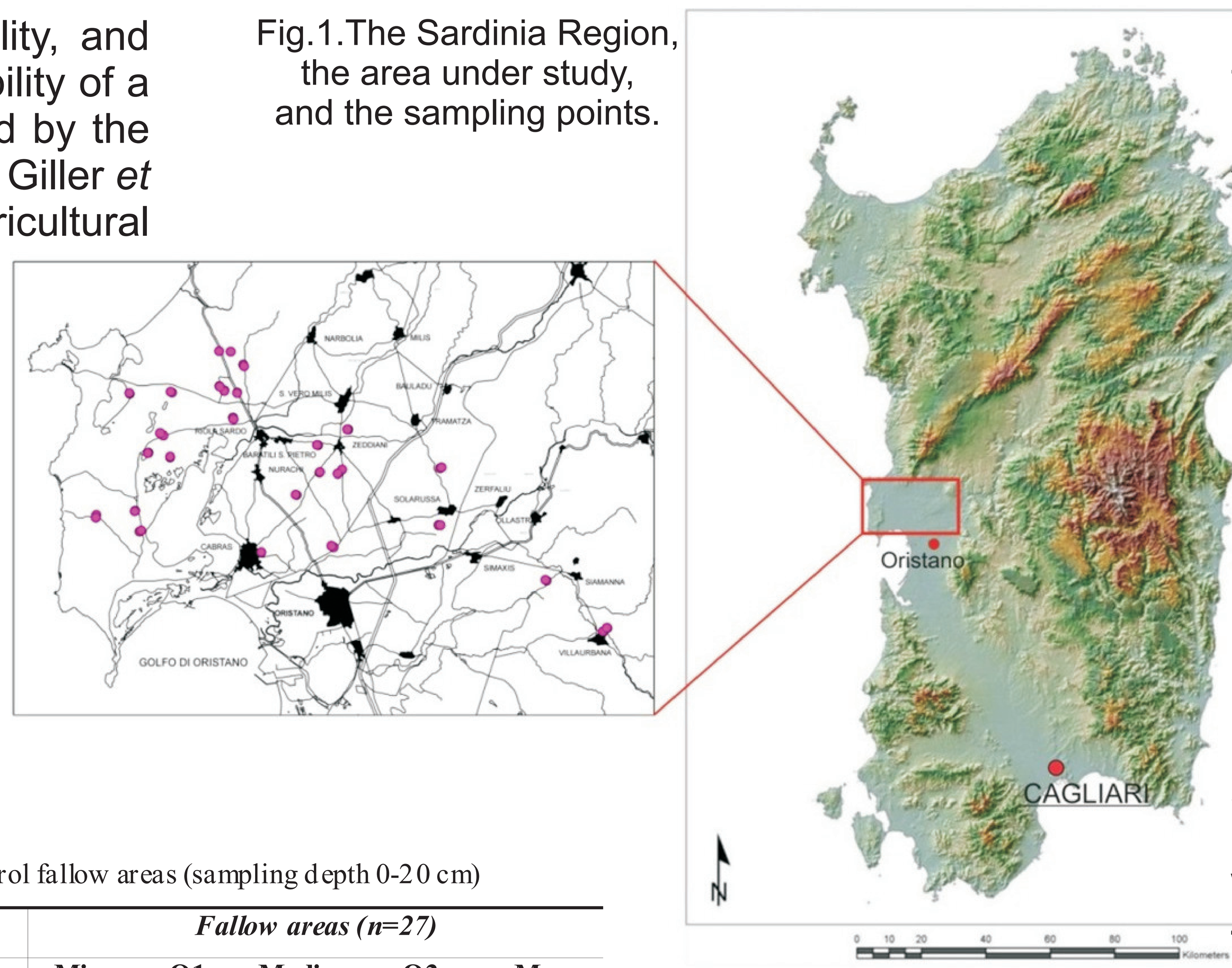

Table 1 Descriptive statistics of the soil property in the tilled and control fallow areas (sampling depth 0-20 cm)

	Tilled areas (n=27)					*Fallow areas (n=27)*				
	Min	Q1	Median	Q3	Max	Min	Q1	Median	Q3	Max
Sand (g kg^{-1})	22.00	364.00	537.00	624.00	819.00	208.00	481.00	575.00	643.00	834.00
Silt (g kg^{-1})	78.00	138.50	166.00	190.00	518.00	10.00	127.50	186.00	250.00	538.00
Clay (g kg^{-1})	82.00	220.50	284.00	364.50	570.00	91.00	203.50	253.00	273.00	426.00
pH (H_2O)	5.58	6.94	7.41	8.24	8.52	6.24	6.83	7.61	8.21	8.53
O.M. %	0.70	1.38	1.74	2.42	3.49	0.88	1.55	2.28	2.67	4.09
Ca^{++} (mg kg^{-1})	369.70	1462.00	2566.00	3356.50	4852.00	523.20	1433.00	2405.00	3548.00	5112.00
Mg^{++} (mg kg^{-1})	38.16	94.78	173.00	273.85	713.50	57.20	126.75	170.00	240.65	763.70
K^+ (mg kg^{-1})	128.20	229.60	345.30	407.25	765.00	65.95	200.50	219.40	295.35	720.00
Na^+ (mg kg^{-1})	8.07	25.05	32.43	55.80	326.00	18.86	29.18	41.04	82.01	195.10
CEC (cmol kg^{-1})	9.50	15.57	20.05	26.68	34.05	7.82	16.04	22.88	27.49	35.91
Bases saturation %	20.30	60.30	72.60	88.30	100.00	41.90	56.85	70.01	81.35	100.00
ECe (dS cm^{-1})	0.12	0.29	0.43	0.55	1.13	0.17	0.35	0.43	0.57	1.07

Experimental layout

The survey was carried out in the west coast of Oristano province (Sardinia, Italy) on an area of about 200 km^2 (Fig. 1). All the investigated territories are listed in the production rules of Vernaccia PDO (Protected Designation of Origin) wine.

Field sampling

The 27 vineyards admitted to the survey were aged between 20 and 50 years. Each sample was collected in four depths: 0-20 cm, 20-40 cm, 40-60 cm, and 60-100 cm when possible, to evaluate the heavy metals distribution along soil profile. Each vineyard was coupled with a fallow area with similar pedological characteristics as a control and samples were analyzed to evaluate the difference between "disturbed" and "undisturbed" soils. Laboratory analysis were performed according to the Italian standard procedures of soil chemical analysis. Soil samples were analyzed for particle-size and chemical parameters (Table 1). The heavy-metal analysis were performed using an ICP-AES Spectroscopy.

Results and discussion

The Italian heavy metal threshold values are referred either to public parks or residential soils (Tab. 2). No values are fixed for agricultural soils. The pseudo-total copper fraction, extracted in *aqua regia* and referred to the tilled soils (0-20 cm), shows a median value of 22.70 mg kg^{-1} and a diminishing trend increasing the sampling depth (Fig. 2). The 60-100 cm depth median copper concentration is equal to 13.84 mg kg^{-1} which is a bit more than half of that found in surface samples (Fig. 2). The data also show a significant difference ($p<0,05$) between the pseudo-total copper concentration on tilled and fallow areas (0-20 cm of depth). The difference become not-significant increasing the sampling depth, so showing an accumulation especially limited to the first 20 cm (Fig. 2, and 3). As regard the available copper fraction (extracted in DTPA), the median value (0-20 cm) found was 3.28 mg kg^{-1}, with a maximum of 21.20 mg kg^{-1} (Fig. 4). Even in this case the data show a significant difference ($p<0,05$) between tilled and fallow areas, limited to the first 0-20 cm of soil. As regards the other heavy metals (Tab. 2), their presence is not voluntarily, and can be due to natural causes. As a matter of fact, the studied area is scarcely urbanized and with no factories or mining activities. The survey showed a low and constant concentration, from 0 to 100 cm, of the other analysed heavy metal (Tab. 2, and 3), which could confirm their natural origin. Moreover, the observed differences between tilled and fallow areas were statistically not-significant both for pseudo-total and available fractions. No values higher than the thresholds have been found, except for cobalt, found greater than its legal limit on one vineyard and its control (Tab. 2).

Conclusions

Despite the studied vineyards had received copper treatments from 20 to 50 years, our data show that the use of copper-based fungicides in the long-term vineyards do not represent a cause of concern for the studied areas, as perfectly capable of ensuring environmental sustainability in the long period.

Table 2 Descriptive statistic of pseudo-total heavy metals fractions (sampling depth 0-100 cm)

Heavy metals mg kg^{-1}	Soil(1)	Min	Max	Q_1	Median	Q_3	Average	St. Dev (n-1)	CV	Threshold values(2) mg kg^{-1}
				Pseudo-total fraction (n=82)						
Mn^{++}	T	89.11	542.00	194.55	268.35	398.00	292.68	121.36	0.41	-
	F	66.18	583.45	197.64	288.69	371.42	297.95	118.87	0.40	
Co^{++}	T	2.50(3)	23.89	2.50(3)	7.47	10.37	7.63	4.80	0.63	20
	F	2.50(3)	25.06	5.41	7.78	10.29	8.06	4.61	0.57	
Cu^{++}	T	5.00(3)	80.18	10.36	15.96	23.50	18.94	13.93	0.73	120
	F	5.00(3)	54.24	5.00(3)	14.08	17.82	15.14	10.36	0.68	
Zn^{++}	T	7.68	122.56	33.00	44.42	58.99	48.04	22.30	0.46	150
	F	13.71	107.00	33.33	44.06	57.34	47.06	19.08	0.40	
Pb^{++}	T	5.00(3)	22.37	5.00(3)	5.00(3)	12.28	8.86	4.60	0.52	100
	F	5.00(3)	31.48	5.00(3)	5.00(3)	12.73	9.28	5.42	0.58	
Cr^{++}	T	5.00(3)	82.28	14.07	20.37	29.22	23.40	15.67	0.67	150
	F	5.00(3)	74.54	13.80	20.49	27.17	23.32	14.68	0.63	
Ni^{++}	T	5.00(3)	59.98	5.00(3)	11.19	16.76	13.45	12.22	0.90	120
	F	5.00(3)	58.94	5.00(3)	11.99	15.99	13.62	10.94	0.80	
Cd^{++}	T	2.50(3)	2.50(3)	2.50(3)	2.50(3)	2.50(3)	2.50(3)	0.00	0.00	120
	F	2.50(3)	2.50(3)	2.50(3)	2.50(3)	2.50(3)	2.50(3)	0.00	0.00	

(1) Tilled area/Fallow area
(2) Annex 5 D.lgs 152/2006
(3) Estimate value equal to LOD/2

Table 3 Descriptive statistic of available heavy metals fractions (sampling depth 0-100 cm)

Heavy metals mg kg^{-1}	Soil(1)	Min	Max	Q_1	Median	Q_3	Average	St. Dev (n-1)	CV
				Available fraction (n=82)					
Mn^{++}	T	0.72	46.40	6.53	10.38	22.35	14.59	10.54	0.72
	F	0.87	302.00	5.85	11.18	25.15	19.47	34.26	1.75
Cu^{++}	T	0.10	21.20	0.65	1.54	3.21	2.95	4.02	1.35
	F	0.10	14.20	0.38	0.81	1.89	1.49	2.15	1.43
Zn^{++}	T	0.02	3.44	0.25	0.49	0.85	0.72	0.71	0.99
	F	0.08	4.00	0.20	0.36	0.93	0.71	0.82	1.14
Ni^{++}	T	0.01	3.16	0.47	0.91	1.35	1.00	0.65	0.64
	F	0.09	6.70	0.43	0.97	1.45	1.11	0.92	0.82
Pb^{++}	T	0.01	4.02	0.29	0.50	0.90	0.72	0.79	1.09
	F	0.08	4.36	0.28	0.59	0.97	0.76	0.77	1.01
Cd^{++}	T	0.01	0.34	0.01	0.03	0.04	0.04	0.05	1.23
	F	0.01	0.14	0.01	0.02	0.04	0.03	0.03	0.88

(1) Tilled area/Fallow area

Fig.2.Pseudo-total Cu^{++} concentration (mg kg^{-1}). Tilled areas

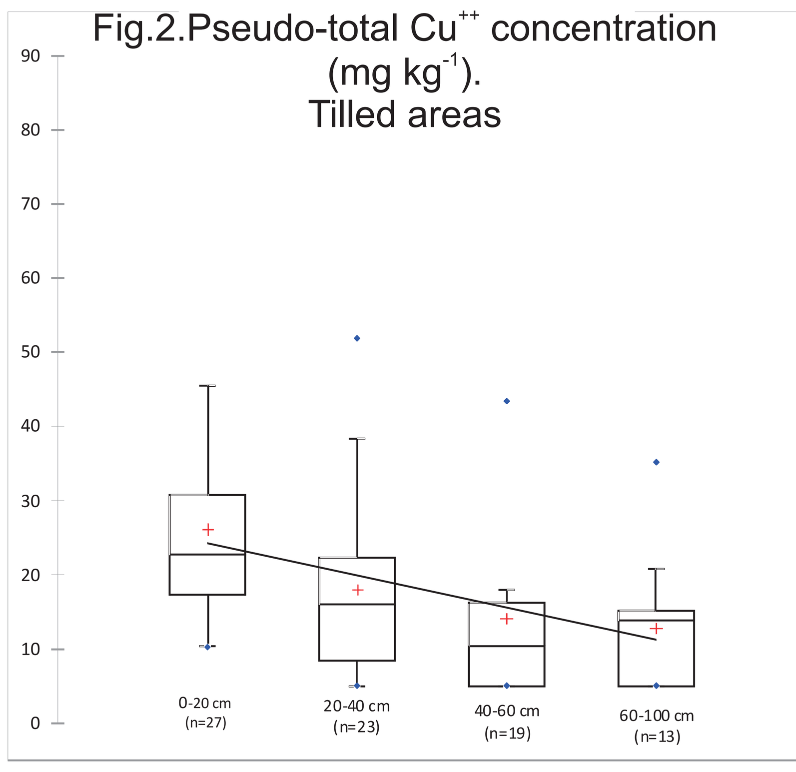

Fig.3.Pseudo-total Cu^{++} concentration (mg kg^{-1}). Fallow areas

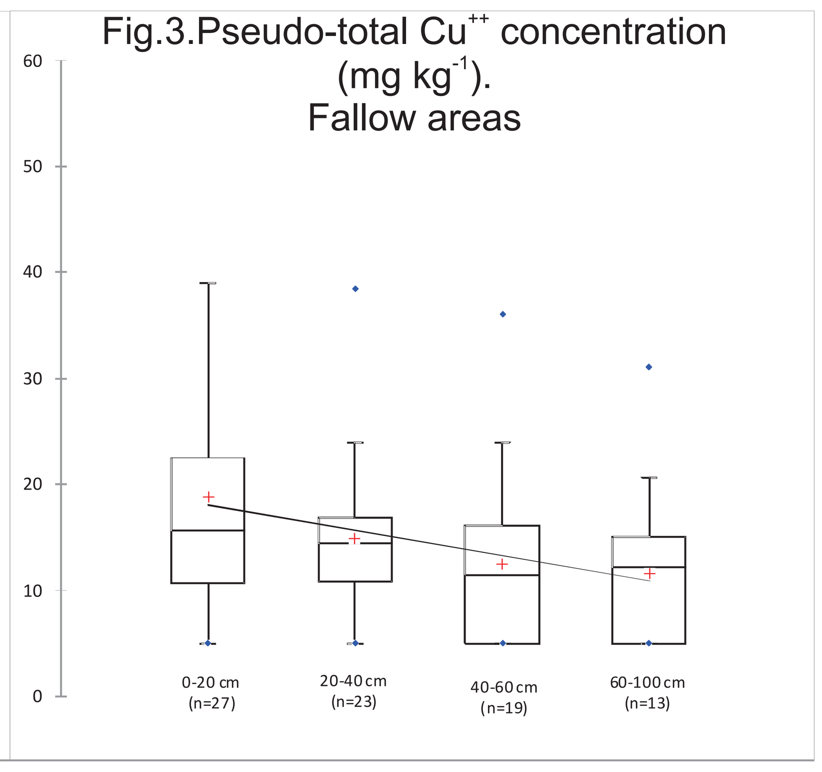

Fig.4.Available Cu^{++} concentration (mg kg^{-1}). Tilled areas

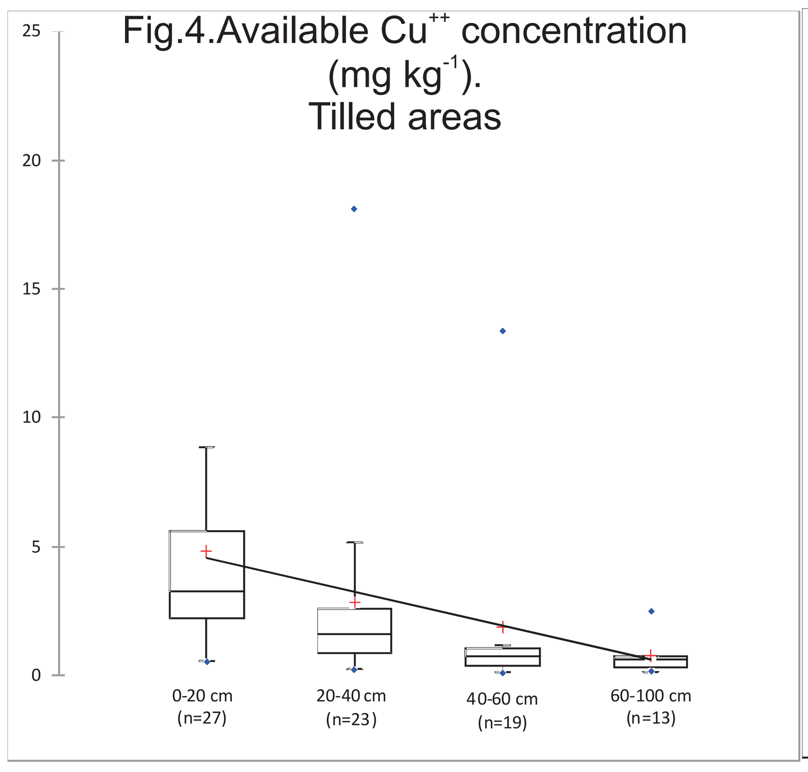

Fig.5.Available Cu^{++} concentration (mg kg^{-1}). Fallow areas