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Trace metals in wine and vineyard environment in southern Ukraine

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ABSTRACT

The study was focused on measuring the concentration levels of trace metals in the environment, vines and wine within the wine-growing region of Ukraine and comparing the findings to the data from well known wine-growing areas. Analysis was carried out of Cr, Cu, Ni, Pb and Zn in irrigation water, grape juice and wine, Cu, Pb and Zn in soil (pseudo-total and acid-soluble fractions) and *Vitis vinifera* L. in leaves and grapes. The accumulation levels of Cu and Zn from soil to leaves were significantly higher than from soil to grapes. Pb had lower potential to accumulate in aerial parts than Cu and Zn. Higher contents of Cu and Zn were observed in Muscat white grape juice compared to Chardonnay. The concentration levels of Zn and Cu were higher in wine than in juice. Trace metals were regulated by the soil composition and biological specificity of cultivars. The data obtained from the study area did not exceed the international limits.

1. Introduction

Wine has been a popular and widely-consumed alcoholic beverage worldwide since early civilization (Kostic, Mitic, Miletic, Despotovic, & Zarubica, 2010; Tariba, 2011). The quality, origin, aroma/flavor characteristics and health safety of wine consumption (Fiket, Mikac, & Kniewald, 2011; Kostic et al., 2010) are influenced by environmental and anthropogenic factors and can be identified by varying contents of inorganic and organic substances forming its chemical composition (Kostic et al., 2010). Environmental factors are geography (e.g. region, orography, presence of water resources), climate (e.g. temperature, precipitation, humidity, wind, etc.), soil type and composition and grape variety (Fiket et al., 2011; Kostic et al., 2010). Among the anthropogenic factors, principle impacts are associated with the pollution of vineyards (e.g. soil contamination and irrigation water quality) (Fernandez-Calvino, Rodriguez-Suavez, Lopez-Periago, Arias-Esteve & Gandara, 2008), viticulture management practices such as use of seed preservatives, chemical sprays, fertilisers, grape-growing approaches (Chaignon, Sanchez-Neira, Herrmann, Jaillard, & Hinsinger, 2003; Chopin et al., 2008), and winemaking technology and storage (Tariba, 2011). Hence, the contamination of wine by trace metals may occur at different steps of vine-growing (Al Nasir, Jiries, Batarseh, & Beese, 2001; La Pera et al., 2008; Fiket et al., 2011), due to the application of agricultural chemicals; winemaking and ageing (Chaignon et al., 2003), because of extended contact of wine with winemaking equipment materials (aluminium, brass, glass, stainless steel and wood, etc.) (Tariba, 2011). The analysis of certain metals in wines is of special interest due to toxicity in the case of excessive intake, effect on organoleptic properties (Lara, Cerutti, Salonia, Olsina, & Martinez, 2005) and use for the description and classification according to the geographical origin and assessment of authenticity (Rodriguez et al., 2011; Tariba, 2011).

The winemaking history of Ukraine started in ancient times and passed periods of development (1860–1980), destruction (1980–1988) and restoration (1989 – present time) (Rybentsev, 1995). Ukrainian vine-growing areas are mainly located in southern (Crimea and Odessa) and western (Carpathian) regions. The total area of vineyards in Ukraine is c.a. 75,000 ha. The current challenges of vine-growing and winemaking in Ukraine are the: (i) weak wine authentication systems; (ii) absence of relevant environmental and health security standards for the control of local vineyards and final products; and (iii) continuous reduction of local cultivars that are adapted to specific climate conditions and growth of foreign cultivars, resulting in the increasing the use of agricultural chemicals. Unfortunately, a small amount of data on trace metals concentration levels of Ukrainian wines and vineyards can be found in available scientific publications.

In order to obtain the first overview on trace metals in the Ukrainian vineyard environment, vines and wine, our study focused on the investigation of potentially toxic trace metals (Cr, Cu, Ni, Pb and Zn) in the environment of the southern viticulture region and young wines from the Sevastopol area of Crimea. The objectives of the study were to: (i) determine trace metals in irrigation water, soil, grapes, vine leaves, grape juice and young wines (after fermentation); (ii) indicate potential routes of trace metals in

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wine; and (iii) compare obtained data with previous studies and current wine quality limits.

2. Materials and methods

2.1. Study area

The studied vine-growing site is located in the Sevastopol area, South Crimea (44°33′13.82″N 33°39′18.22″E) (Fig. 1). Geologically this area belongs to the southwestern edge of the Crimean Mountains – an element of the Mediterranean fold belt. The bedrock consists of Triassic layers of conglomerate, sandstone, siltstone and argillite. Reliefs were formed mainly by processes of surface water erosion. The vineyard is situated in the valley of the Chorna River, which is used for the irrigation of the vines. The region has a temperate continental climate with elements of the subtropical Mediterranean, a mean annual temperature of +12 °C and annual precipitation of 360 mm.

The southern vine-growing region of Sevastopol is located near the closed soviet military bases of Balaklava, which are still used for the explosive disposal of old ammunition and are surrounded by the railway, motorway, local settlements and agricultural territories. The study area (72 ha) is used for the growing of vine cultivars (cv.) Chardonnay and Muscat white for the production of popular sparkling wines in Ukraine, and has been cultivated since 2007.

The soil of the region is a Calcic Fluvisol (Clay Loamic) (WRBSR, 2007), what shows alkaline pH (8.1 ± 0.2), high $CaCO_3$ content (30 ± 5%) with active carbonates of 11–16%, mobile nutrients (mean value in the 0–60 cm layer), nitrate nitrogen is 6–11 mg kg^{-1} and K_2O is 220–280 mg kg^{-1}. Within a sample plot there were no significant variations in the content due to the deep ploughing (60 cm) and rotation of the soil layer prior to the vine plantation.

About 3400 kg per year of agricultural chemicals (c.a. 47 kg per ha), mainly fungicides (e.g. penconazole, propiconazole, metalaxyl, mancozeb etc.), are applied to protect the crops.

2.2. Reagents and solutions

Standard solutions were prepared by the dilution of analytical standards (1000 mg L^{-1}) obtained from the State Standard Solutions of Ukraine (Instructions, 1992; Giokas, Eksperiandova, Blank, & Karayannis, 2004). Grade metal solutions (BDH, Poole, Dorset, UK) were used for atomic adsorption spectroscopy with a flame atomizer (FA-AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). All metal solutions were of the highest purity to ensure minimal errors (Giokas et al., 2004). Merck Suprapur® HNO_3 (65%) was used for the stabilization of the standard solutions and natural samples. NaOH (30%, Merck Suprapur®) and HCl (32%, Reidel) were used for the pH adjustment of the solutions. Certified standards SLRS-4 (water), CRM 320 and IAEA 405 (riverine sediments) were used for the inductively coupled plasma mass spectrometry (ICP-MS) analysis of water and sediments samples (Vystavna et al., 2012).

2.3. Sampling and samples preparation

The sampling was carried out from August–September 2012, one week before harvesting. The study included the sampling of: (i) water (number of samples, $n = 6$) and sediments ($n = 6$) of the Chorna River; (ii) topsoil of the vineyard ($n = 8$); grapes ($n = 8$)

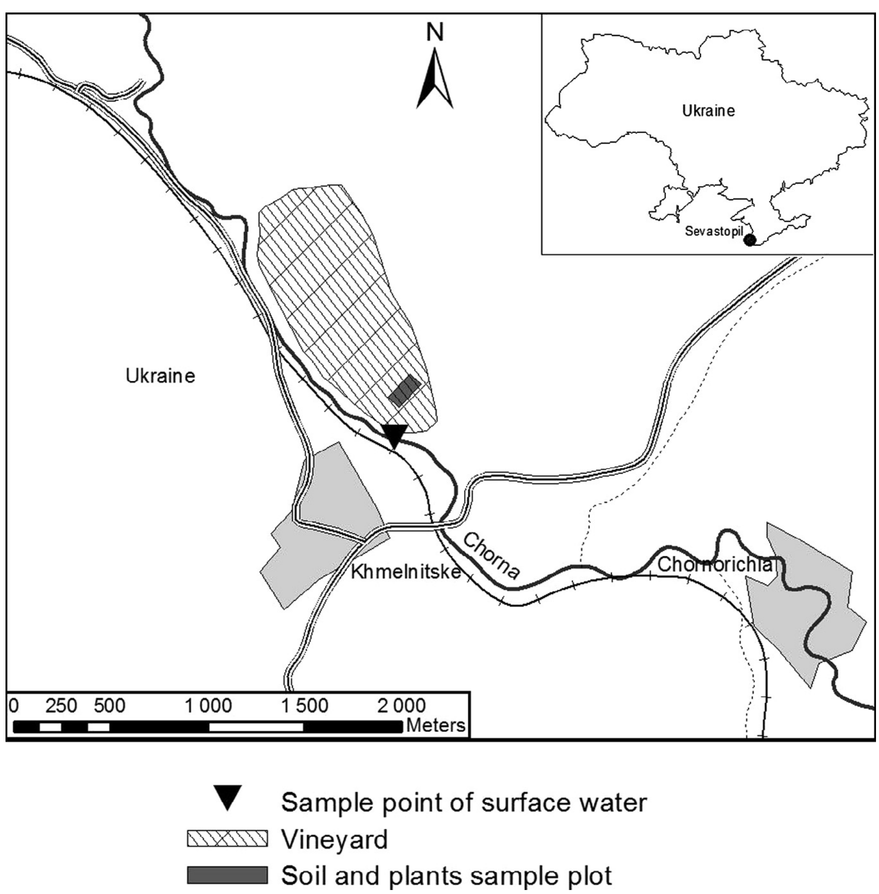

Fig. 1. Location of the study area.