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Bioavailability of potentially toxic elements in soil–grapevine (leaf, skin, pulp and seed) system and environmental and health risk assessment

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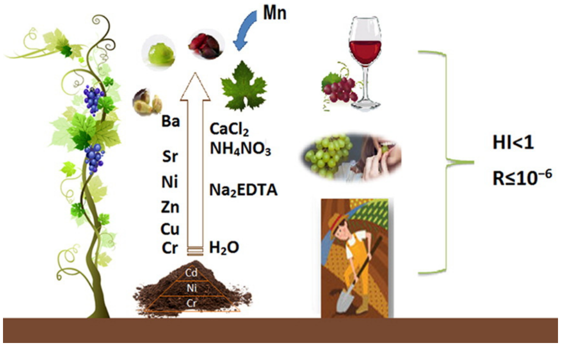
HIGHLIGHTS

- Bioavailability of the toxic element for grapevines and consumers was considered.
- Element concentrations were measured in soil and different grapevine parts.
- Six single extraction procedures isolated different portion of elements from soil.
- Ba was easy bioavailable; Cu and Zn were mostly accumulated in seed and leaf, respectively.
- Non-carcinogenic and carcinogenic risks were low for workers and grape consumers.

GRAPHICAL ABSTRACT



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ABSTRACT

Monitoring of potentially toxic elements in agricultural soil represents the first measure of caution regarding food safety, while research into element bioavailability should be a step forward in understanding the element transportation chain. This study was conducted in the grapevine growing area ("Oplenac Wine Route") for investigating element bioavailability in the soil–grapevine system accompanied by an assessment of the ecological implications and human health risk. Single extraction procedures (CH_3COOH, Na_2EDTA, $CaCl_2$, NH_4NO_3 and deionised H_2O) and digestion were performed to estimate the bioavailability of 22 elements (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sr, V and Zn) from the topsoil (0–30 cm) and subsoil (30–60 cm) to the grapevine parts (leaf, skin, pulp and seed) and wine. The extractants were effective comparing to the pseudo-total concentrations in following order $Na_2EDTA > CH_3COOH > NH_4NO_3 > CaCl_2$, H_2O 2 h and 16 h. The most suitable extractants for assessing the bioavailability of the elements from the soil to the grapevine parts were $CaCl_2$, NH_4NO_3 and Na_2EDTA, but deionised H_2O could be suitable, as well. The results showed that Ba was the most bioavailable element in the soil–grapevine system. Contamination factor implied a moderate contamination ($1 < CF < 3$) of the soil. The concentrations of Cr, Ni and Cd in the soil were above the maximum allowed concentrations. According to the biological accumulation coefficient (BAC), the grape seeds and grapevine leaves mostly accumulated Cu and Zn from the soil, respectively. Based on ratio factor ($RF > 1$), the influence of atmospheric deposition on the aerial grapevine parts (leaves and grape skin) was observed. Nevertheless, low adverse health risk effects ($HI < 1$ and $R \leq 1 \times 10^{-6}$) were estimated for farmers and grape and wine consumers.

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1. Introduction

The increasing release of agrochemicals into the environment has led to growing public concern over the potential accumulation of pollutants (e.g. potentially toxic elements) in agricultural soil and consequently in plants. In the vineyard soils, a serious impact on the soil pollution could be caused by potentially toxic elements from the chemical fertilisers and pesticides (Kabata-Pendias and Mukherjee, 2007), but also from some other surrounding sources (e.g. industrial activities, traffic). Aside from widely accepted Cu-fungicide treatments, conventional inorganic agrochemicals may also contain some elements (Cd, Cr, Cu, Ni, Pb and Zn) as impurities (Thomas et al., 2012).

Determination of the potentially toxic elements in agricultural soil is of the great importance because the increased values of these elements could cause environmental and health implications (soil pollution, inhibition of plant growth, a health risk for workers and consumers, etc.). Distribution of the elements in the soil and their bioavailability from soil to different parts of grapevine (further referred as bioavailability) depends on the reactions of elements in soils such as mineral precipitation and dissolution, ion-exchange, adsorption and desorption, aqueous complexation, biological immobilisation and mobilisation, and plant uptake (Wuana and Okieimen, 2011). Human activities can increase the content of pollutants up to the phytotoxic level. In addition, for workers in the fields, who are chronically exposed to potentially toxic elements from the soil and directly exposed during agrochemical spraying treatments, these elements could cause serious health consequences (poisoning, respiratory diseases, even carcinogenic diseases). The elements in soils may affect human health through the inhalation of dust, ingestion of soil, or by dermal contact (Sylvain et al., 2016). The increased concentration of potentially toxic elements in soils can cause a potential risk to human health because of their subsequent involvement in the food chain through plant uptake (Islam et al., 2015; Niesiobędzka, 2016). There are different models that can be found and used for calculating human health risk assessment applying the concentrations of measured pollutants in soil samples. The most used in the soil studies (Li et al., 2015; Tepanosyan et al., 2017a; Tepanosyan et al., 2017b; Minolfi et al., 2018) is from US EPA guidance for human health risk assessments and adequate equations can be found at *The Risk Assessment Information System, RAIS* (RAIS, 2013). These equations were used in this study (RAIS, 2013). Besides this model, there are CLEA (contaminated land exposure assessment) and CSOIL models and etc. Most of them deal with calculations of humans risk by exposure to contaminated soil via different routes. CLEA and CSOIL calculate the maximum concentration of contaminants that are safe for humans and used by UK and Dutch Environmental National Agencies.

Investigation of element bioavailability from contaminated agricultural soil receives attention at the international level and has been ongoing for more than few decades (Pelfrêne et al., 2012). The single extraction procedures are generally recommended and widely used for studying the bioavailability of major and trace elements from agricultural soils and for predicting their influence on plants. The single extraction procedures most often applied are those with Na_2EDTA, NH_4NO_3, $CaCl_2$ and deionised H_2O as extractants. The single extractions are simple procedures, which give information on the assessment of the "labile" elements in soils (Santos et al., 2010) and the procedure applying deionised H_2O is eco-friendly and cost-effective, as well. Nowadays, different extraction procedures are included in national and international regulations, or they have been considered in the framework of normalisation bodies such as CEN or ISO (Quevauviller et al., 1996).

According to the available literature, there are not many studies that compare all the mentioned single extraction procedures with pseudo-total digestion for assessing the bioavailability of potentially toxic elements in the soil–plant system (Niesiobędzka, 2012). There are studies in which two or three single extraction procedures were compared. For example, aqua regia and Na_2EDTA procedures were usually applied in studies for determining an environmental risk assessment, while 0.05 mol L^{-1} Na_2EDTA procedure was presented in studies as an agent that by the complexation process simulate the uptake of available element fraction from soil. Weak salt solutions ($CaCl_2$ and NH_4NO_3) could only be used as extractants for elements presented in the exchangeable phase and the water-soluble phase (Pinto et al., 2015), and together with deionised H_2O as extractants, they were usually applied in soil–plant uptake studies. Unbuffered mild extractants such as $CaCl_2$, NH_4NO_3 extract the exchangeable fraction of the elements and these extractants simulate soil pore water (Quevauviller et al., 1996; Pueyo et al., 2004). Acid reagents such as CH_3COOH assess the fraction of the elements remobilised by an acidification process. Aqua regia and 0.01 mol L^{-1} $CaCl_2$ were used to determine soil fertility (Quevauviller et al., 1996; Pueyo et al., 2004; Ettler, 2016).

In this comprehensive study, for the first time, all the mentioned single extraction procedures were applied in a commercial vineyard area for predicting the bioavailability of potentially toxic elements from the soil to different grapevine parts (leaf, skin, pulp and seed). The main aim of this study was to assess the bioavailability of potentially toxic elements from topsoil and subsoil to different grapevine parts by simultaneously testing six single extraction procedures (CH_3COOH, Na_2EDTA, $CaCl_2$, NH_4NO_3 and deionised H_2O during 2 h and 16 h). In addition, the ecological implications and health risk implications of the potentially toxic elements were estimated for workers in the vineyard, consumers of the grapevine (adults and children) and the wine (adults).

2. Materials and methods

2.1. Study area

The study was conducted in the agricultural area "Oplenac Wine Route" (44°13′36.3″ N 20°39′12.4″E), well-known for grapevine growing in Serbia and the region. The sampling sites were located in the village, near the town of Topola, 80 km from Belgrade, the capital of Serbia. Six vineyard parcels were investigated. The potential pollution sources (metal foundry near parcel VI and the main road near parcels I, IV and V) were identified close to the investigated vineyard area. The highest distance between the parcels was 2 km (between parcels IV and V). The parcels I, II, III were located next to each other and they were separated from the parcel IV by the road. The parcel V is 800 m distance from the parcel VI. The studied soils are alluvial colluvial (Coluvic Regosol). It is very carbonated, sandy clay and poorly humus soil (Ninkov et al., 2014). The studied parcels were in the system no-tilling grapevine production (without soil-tilling process) and they were not located on sloping terrain. In the studied region, precipitations were the most frequent in March and June (before the harvest) in 2015 (Republic Hydrometeorological Service of Serbia), (Fig. 1).

2.2. Sampling

The sampling was performed during the grapevine harvest of 2015. Topsoil (0–30 cm) and subsoil (30–60 cm) samples (n = 54), leaf samples (n = 26) and grapevine samples (n = 104 – seed n = 26, pulp n = 26, skin n = 26, whole berries n = 26) were collected from six vineyard parcels (I – samples 1–5; II – samples 6, 7; III – samples 8, 9; IV – samples 10–14; VI – samples 15–18, and V – samples 19–26). The soil samples from two depths were collected because most roots are found within the top 1 m (personal communication, 2015). The soil samples were collected using the sampling probe, following the protocol reported by the Institute of Field and Vegetable Crops, Novi Sad, Serbia (http://www.nsseme.com/en/). Approximately 1 kg of each soil sample was collected in plastic bags. The control location (C) for the determination of the local background values of the measured elements in the soil was located in the same area, in the surrounds of the grapevine growing parcels but not exposed to any agricultural activities or plant growth. Two grapevine species were sampled in the vineyard, *Sauvignon blanc* from parcels I, II, III, IV and VI; and *Cabernet sauvignon* from parcel V.