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Grapevine accumulation of potentially toxic elements from soil: Health risk and implication assessment

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Abstract This study was performed in a commercial vineyard. Topsoil (0 – 30 cm) and two grapevine species (*Cabernet sauvignon* and *Sauvignon blanc*) samples were collected. The concentrations of Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, V, Zn were determined. Bioavailabilable elements from soil were established applying single extraction methods (CH_3COOH, Na_2EDTA, $CaCl_2$, NH_4NO_3 and deionised water) and pseudo-total digestion. The accumulation of potentially toxic elements in leaves, seed, pulp, and skin of the grapevine was assessed. Health risk for farmers and hazardous index for grape consumers were estimated. The most suitable extractants for isolating concentrations of Ni and Sr bioavailable for leaf were $CaCl_2$ and NH_4NO_3. The concentrations of Cu and Ni bioavailable for seed were extracted by deionised water – 2 h extraction. The most suitable extractant for isolating bioavailable Sr and Zn for skin was Na_2EDTA; for Ni and Sr it was $CaCl_2$; for Fe and V it was deionised water – 16 h extraction. Health risk assessment showed noncarcinogenic risk for farmer's exposure to the soil, and slightly carcinogenic risk was indicated. The hazardous index showed that both grapevine species were safe for consumption.

Keywords: trace elements, bioavailability, single extractions, pseudo-total digestion, (non)carcinogenic risk

1. Introduction

Nowadays, foodborne diseases have a major impact on human health. Pesticides are a significant cause of foodborne illness, although effects are often difficult to link with a particular food or agricultural area. Besides, the soil contamination is a widespread problem all around the world. Contaminants in agricultural soil and plants usually include fertilizers and pesticides (WHO, 2014). One of the most important steps in preventing contamination of agricultural products is monitoring of major and trace element content, which presented in excess could be toxic. Variations of the physico-chemical properties of potentially toxic elements as well as soil can influence the release of these elements (Filgueiras *et al*., 2002). The presence of potentially toxic elements in soils and plants may affect human health through the inhalation of dust, ingestion of soil, dermal contact, or consuming products from the agricultural field (Morel *et al*., 1997; Kabata – Pendias and Pendias, 2001). The acidity (pH) is of the particular importance because it controls the behavior of potentially toxic elements. This experiment was performed to investigate bioavailabile fractions of potentially toxic elements from vineyard soil, and their accumulation in different parts of grapevine (seed, skin, pulp and leaf). In addition, potentially hazardous effects on the environment and people have been investigated in the vineyard region applying environmental and health risk assessment formulas.

2. Methods

The "Oplenac Wine Route" is a well-known region for vine growing in Serbia, near "Topola" city, 80 km away from Belgrade. The topsoil (0 – 30 cm), grape leaves and grapevine were collected from 22 sampling sites in the vineyard (along six parcels), during the grapevine season of 2015. *Cabernet sauvignon* was growing at the one parcel (sampling sites 15 - 18) while the another species was *Sauvignon blanc* at the other parcels (1-14 and 16-22). Bioavailable elements from the soil samples were extracted with five different single extraction procedures: 0.11 mol L^{-1} CH_3COOH during 16 h extraction; 0.01 mol L^{-1} $CaCl_2$ during 3 h extraction; 1 mol L^{-1} NH_4NO_3 during 2 h extraction; and distilled water during 2 h (Pueyo *et al*. 2004; Quevauviller, 1998) and 16 h (Milićević *et al*, 2017). Distilled water extraction of 16 h was tested as an alternative to single extraction procedures for isolating bioavailable toxic elements from the vineyard soils. The leaf and grape samples were digested in a microwave digester (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy), with aqua regia (1 mL of 30% H_2O_2 and 7 mL of 65% HNO_3).

The concentrations of 23 potentially toxic elements (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, V, and Zn) were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6500 Duo, Thermo Scientific, UK) and inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Scientific iCAP Q, Thermo Scientific, UK). The special attention was given to the investigation of some potentially toxic elements to plant, which could originate from fertilizers, pesticides, and other anthropogenic sources (As, B, Cu, Fe, Ni, Sr, V, and Zn). For data analysis, SPSS software version 21 for Windows and Statistica 8 (StatSoft Inc., Tulsa, OK, USA) were used. Correlation and multivariate analysis (PCA) were used to identify specific correlations between the element concentrations. Normality of the data was tested by the Kolmogorov–Smirnov test.

Contamination factor (CF) and pollution load index (PLI) were calculated to investigate the level of soil contamination by potentially toxic elements (Likuku *et al*., 2013).

Applying the formulas available at *The Risk Assessment Information System, RAIS*, potential and carcinogenic risks were calculated for farmer's exposure to the soil during grapevine season (6 months, 8 h per day). In addition, potential risk was determined for consumers of the grapevine species (176 g day^{-1}).

3. Results and Discussion

3.1. Bioavailability of elements in system soil-different plant parts (leaf, skin, seed, and pulp)

The acidity of the soil samples in all analysed parcels was in the range 6.33 – 6.92 (pH KCl) and 6.53 – 7.06 (pH $CaCl_2$). The most suitable extractants for isolating concentrations of Ni and Sr taken up by the leaf (Figures 1e, f) were $CaCl_2$ and NH_4NO_3. The correlation between concentrations of these elements between the leaf and soil were significant at $p<0.01$ (Ni_{leaf}–Ni_{CaCl2}: R=0.74; Ni_{leaf}–Ni_{NH4NO3}: R=0.58; Sr_{leaf}–Sr_{CaCl2}: 0.72; Sr_{leaf}–Sr_{NH4NO3}: 0.47). In addition, for extracting Cu taken up by the leaf (Figure 1c), the best extractant was Na_2EDTA, and for extracting Zn (Figure 1i) it was deionised water during 2 h (Cu_{leaf}–$Cu_{Na2EDTA}$: R=0.40 and Zn_{leaf}–Zn_{2hH2O}: R=0.44, at $p<0.05$).

The concentrations of Cu and Ni taken up by the seed (Figures 1c, e) were the most efficiently extracted by deionised water during 2 h (Cu_{seed}–Cu_{2hH2O}: R=0.65, $p<0.01$; Ni_{seed}–Ni_{2hH2O}: R=0.46, $p<0.05$). In addition, Ni from soil is mobile at pH 4.5–6.5, and it is easy bioavailable to leaves and seeds (Pendias and Mukherjee, 2007). The concentrations of Fe taken up by the seed (Figure 1d) was mostly extracted by the Na_2EDTA (Fe_{seed}–$Fe_{Na2EDTA}$: R=0.43, p<0.05).

For isolating Sr bioavailable to the pulp (Figure 1f), there were few suitable extractants – deionised water during 2 h and 16 h extraction, Na_2EDTA and aqua regia – pseudo-total element content (Sr_{pulp}–Sr_{2hH2O}: R=0.39, $p<0.05$; Sr_{pulp}–Sr_{16hH2O}: R=0.40, $p<0.05$; Sr_{pulp}–$Sr_{Na2EDTA}$: R=0.55, $p<0.01$; Sr_{pulp}–$Sr_{pseudo\text{-}total}$: R=0.42, $p<0.05$). For V (Figure 1g) it was $CaCl_2$, Na_2EDTA and deionised water – 16 h (V_{pulp}–V_{CaCl2}: R=0.47; V_{pulp}–$V_{Na2EDTA}$: R=0.42 and V_{pulp}–V_{16hH2O}: R=0.45, at $p<0.05$), for As (Figure 1a) it was Na_2EDTA and aqua regia (As_{pulp}–$V_{Na2EDTA}$: R=0.44 and V_{pulp}–$V_{pseudo\text{-}total}$: R=0.41, at $p<0.05$). In addition for B and Ni taken up by the pulp (Figures 1b, e) were agua regia (B_{pulp}–$B_{pseudo\text{-}total}$: R=0.61, $p<0.01$; Ni_{pulp}–$Ni_{pseudo\text{-}total}$: R=0.44, $p<0.05$).

The most suitable extractant for isolating bioavailable Sr and Zn taken up by the skin (Figures 1f, i) was Na_2EDTA (Sr_{skin}–$Sr_{Na2EDTA}$: R=0.42 and Zn_{skin}–$Zn_{Na2EDTA}$: R=0.45, at $p<0.05$); for Ni and Sr (Figures 1e, f) it was $CaCl_2$ (Ni_{skin}–Ni_{CaCl2}: R=0.40, $p<0.05$; Sr_{skin}–Sr_{CaCl2}: R=0.83, $p<0.01$); and for Sr (Figure 1f) NH_4NO_3 was suitable (Sr_{skin}–Sr_{NH4NO3}: R=0.46, $p<0.05$); for Fe and V (Figures 1d a, g) it was deionised water – 16 h (Fe_{skin}–$Fe_{16h\ H2O}$: R=0.56, $p<0.01$; V_{skin}–$V_{16h\ H2O}$: R=0.48, $p<0.05$); and for B and Cu (Figures 1b and c) it was agua regia – pseudo-total element content (B_{skin}–$B_{pseudo\text{-}total}$: R=0.42, $p<0.05$; Cu_{skin}–$Cu_{pseudo\text{-}total}$: R=0.42, $p<0.05$). Most of the determined elements are easy or slightly bioavailable at the measured pH of the soil samples.

3.2. Environmental and health risk assessment

The calculated CF indicated moderate ($1 \leq CF \leq 3$), and for a few sites considerable ($3 \leq CF \leq 5$) contamination of the soil in the vineyard (Figure 2), and there were environmental implications for all investigated sampling sites in the vineyard ($1 \leq PLI \leq 2$) by the elements (Figure 3). Thus, these moderate environmental implications could be caused by environmental pollution in the vineyard area, such as fertilizers, pesticides, the proximity of the road or industrial activities near the vineyard.

Health risk assessment implies a non-carcinogenic risk ($\Sigma HI > 0.1$) for farmers who were exposed to the soil during the grapevine season (Figure 4). This implies that analysed the element content in the soil could have a potentially hazardous influence at the farmers who spend all the season working at the fields. In addition, a low carcinogenic risk ($\Sigma R > 10^{-5}$) was calculated for some sampling sites (near the highway road) in the studied vineyard area (Figure 5).

The slightly polluted soil did not influence the hazard index ($\Sigma HI > 1$) for human intake calculated for the grape samples (Figure 6, *Cabernet sauvignon (*15 - 18), and *Sauvignon blanc* (1-14; 16-22). Thus, both studied grapevine species were safe for consumption.

4. Conclusion

After comparasion different single extraction procedures for isolating mobile element fractions and analysing pseudo-total element content in the soil samples, and the grapevine (seed, pilp, skin, leaf), it could be concluded that a unique extractant could not be the best solution for determination of bioavailability of potentially toxic

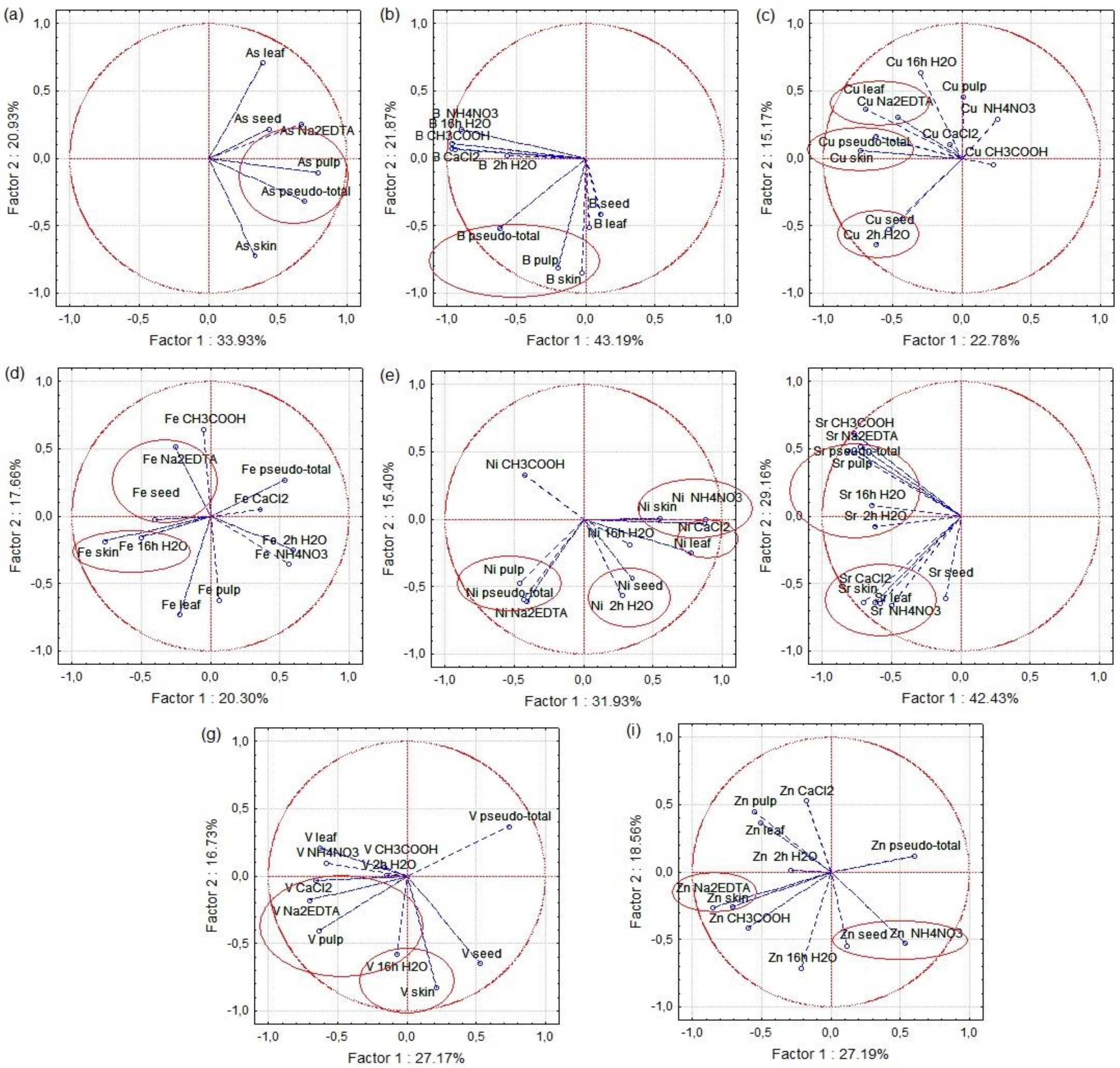


Figure 1. PCA and correlation analysis for testing bioavailability of elements from the soil to the plant parts (a) As; (b) B; (c) Cu; (d) Fe; (e) Ni; (f) Sr; (g) V; and (i) Zn

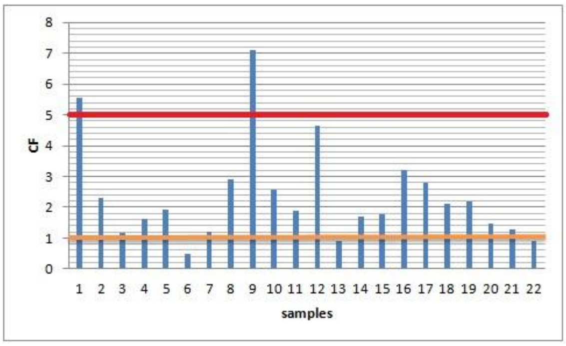


Figure 2 Contamination factor (CF) of the soil samples

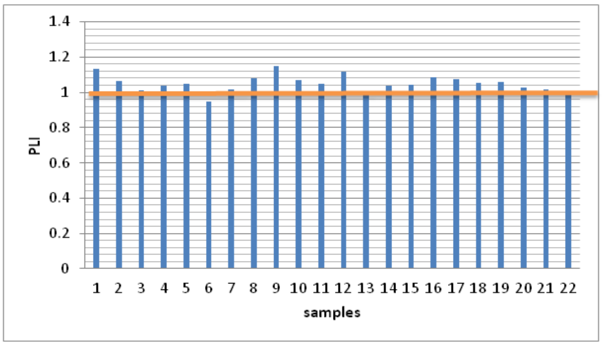


Figure 3. Pollution load index (PLI) of the soil samples

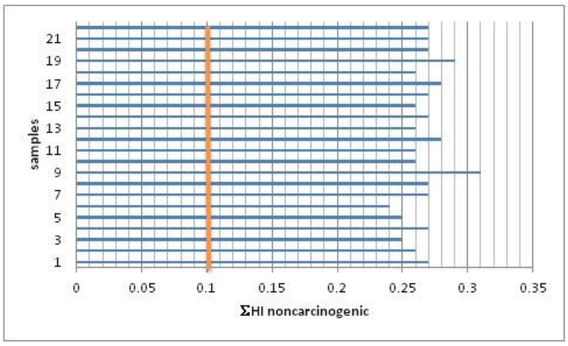


Figure 4 Potential risk for human health influenced by the element content in the soil

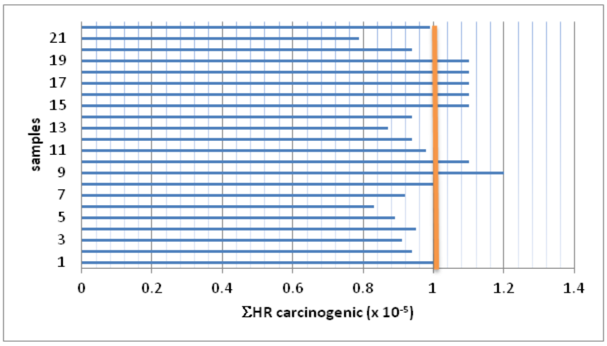
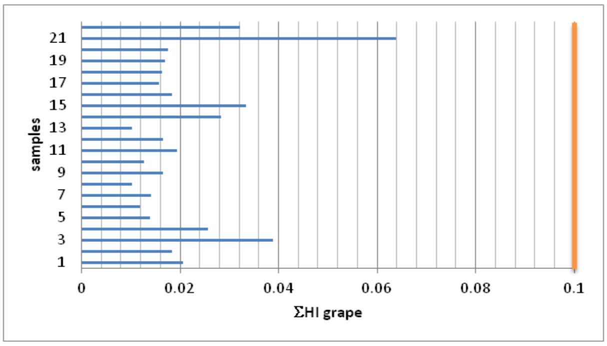


Figure 5. Carcinogenic risk for human health influenced by the element content in the soil



6. Potential risk for human health influenced by the element content in the grape samples

elements in the soil-plant system. However, judging by correlation and PCA analysis, the most suitable extractants, for the vineyard soil were Na_2EDTA, $CaCl_2$, and NH_4NO_3, since most of the element concentrations taken up by the seed, skin, pulp, leaf were significantly in correlated with those concentrations in the extracts. In addition, deionised water was suitable for assessment of some bioavailable elements to seed, skin, and leaves. Deionised water could be useful weak, cost-effective, and environmental friendly soil extraction method for isolating some bioavailable elements from the soil. Ecological risk formulas identified moderate polluted parts of the vineyard influenced by anthropogenic pollution. The health risk assessment indicates some noncarcinogenic risk for workers in the vineyard, but according to the element content, just a few sites in the vineyard were recognized as locations with carcinogenic influence at workers. This implies that there was a potential risk for human health who works in the vineyard fields during the all grapevine season. The fruits of both grapevine species were safe for consumption, which can indicate that the grapevine growth at the ground with not so extreme pollution could be safe for consumption.

References

Filgueiras A. V.; Lavilla I ., Bendicho C., (2002), Chemical sequential extraction for metal partitioning in environmental solid samples. *J. Environ. Monit*., **4**, 823 - 857

Kabata-Pendias and A., Kabata, H. (2001), Trace elements in Soils and Plants, CRC Press, USA.

Kabata-Pendias A. and Mukherjee A., (2007), Trace elements from soil to human, Springer-Verlag Berlin Heidelberg, Germany.

Likuku A.S., Mmolawa K.B., Gaboutloeloe G.K., (2013), Assessment of heavy metal enrichemnt and Degree of contamination around the copper - nickel mine in the Selebi Phikwe region, *Estern Botswana, Env. and Ecol. Res.* **2**, 32 - 40.

Milićević T., Relić D., Škrivanj S., Tešić Ž, Popović A., (2017), Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion, *Chemosphere*, **171**, 284 -293.

Morel J.L., (1997), Bioavailability of Trace Elements to Terrestrial Plants. In: Tarradellas, J., Bitton, D. (Eds.), *Soil Ecotoxicology 6. CRC. Lewis Publishers, Boca Raton*, 141 – 175.

Pueyo M., López-Sánchez J.F., Rauret G., (2004), Assessment of $CaCl_2$, $NaNO_3$ and NH_4NO_3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils, *Anal. Chim. Acta*, **504**, 217 – 226.

The Risk Assessment Information System, *(RAIS) rais.ornl.gov*

Quevauviller Ph., (1998), Operationally defined extraction procedures for soil and sediment analysis, II. Certified reference materials. *Trends Anal. Chem.* **17**, 632-642.

World Health Organisation (*WHO*), *http://www.who.int/topics/food_safety/en/*