UNIVERSITY OF BELGRADE
FACULTY OF CHEMISTRY

Tijana D. Milićević

An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil–plant–air system: bioavailability and biomonitoring

Doctoral Dissertation

Belgrade, 2018

УНИВЕРЗИТЕТ У БЕОГРАДУ

ХЕМИЈСКИ ФАКУЛТЕТ

Тијана Д. Милићевић

Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг

докторска дисертација

Београд, 2018

Belgrade, December 2018

The commission members for the evaluation of the doctoral dissertation:

_____

Dr. Aleksandar Popović, full professor

Faculty of Chemistry, University of Belgrade, Serbia

mentor

_____

Dr. Mira Aničić Urošević, associate research professor

Institute of Physics Belgrade, University of Belgrade, Serbia

mentor

_____

Dr. Dubravka Relić, assistant professor

Faculty of Chemistry, University of Belgrade, Serbia

_____

Dr. Vladimir Beškoski, associate professor

Faculty of Chemistry, University of Belgrade, Serbia

_____

Dr. Gordana Vuković, assistant research professor

Institute of Physics Belgrade, University of Belgrade, Serbia

The commission members for the defence of the doctoral dissertation:

_____

Dr. Aleksandar Popović, full professor

Faculty of Chemistry, University of Belgrade, Serbia

mentor

_____

Dr. Mira Aničić Urošević, associate research professor

Institute of Physics Belgrade, University of Belgrade, Serbia

mentor

_____

Dr. Dubravka Relić, assistant professor

Faculty of Chemistry, University of Belgrade, Serbia

_____

Dr. Vladimir Beškoski, associate professor

Faculty of Chemistry, University of Belgrade, Serbia

_____

Dr. Gordana Vuković, assistant research professor

Institute of Physics Belgrade, University of Belgrade, Serbia

_____

Dr. ir. Roeland Samson, professor

Department of Bioscience Engineering, University of Antwerp, Belgium

Acknowledgements

In the very beginning, I would like to express my very great appreciation to my mentors, Aleksandar Popović and Mira Aničić Urošević for scientific, intellectual and amicable guidance during my doctoral studies. They provided me an excellent atmosphere for doing research and gave me trust, encouragement, amasing enthusiasm during my doctoral studies and they were mentors that every student can only wish.

Although Dubravka Relić is not formally a mentor in this commission, she has definitely been that during the last four years while I was working on my doctoral dissertation. I would like to thank her for the scientific knowledge that she shared with me and her valuable advices, guidelines she provided and finally for supporting and encouraging me all these years.

I would like to extend my thanks to other members of my defence commission, Gordana Vuković, for very useful remarks and suggestions during the writing of the published articles; Roeland Samson, who gave me first insights into magnetic monitoring and enabled me to spend time in his laboratory and to master technique of magnetic measurements; Vladimir Beškoski for contributing in work of the commission.

I would like to show appreciation to wineries "Aleksandrović", "Plavinci" and "Experimental field Radmilovac" for allowing me to conduct experiments in their vineyards. My special thanks go to Vlado Juričić, a viticulturist who gave me the main professional guidelines for organising experimental set up. Also, I am thankful to Branislav (owner of the organic winery), workers from "Aleksandrović" winery and Miroslav for technical support.

Special thanks go to Sandra Škrivanj and Jovana Orlić for assisting me with time-consuming chemical analyses, and to Dragica Nikolić from Institute of Meat, Hygiene and Technology. Thanks go to professor Roeland's laboratory staff for all guidelines and advices during my stay in their laboratory (especially for Ana). In addition, I express great gratitude to Rylant Frank, from ERASMUS office at Antwerpen University and Milorad Milošević from University of Antwerp, for support the realisation of my professional stay in Belgium by Erasmus+ programme. I am grateful to Zoran Mijić, the head of Environmental Physics Laboratory, for useful comments on the final version of dissertation.

Finally, this doctoral dissertation I dedicate to my family and I am grateful to them for support, patience and understanding during my education. Without their support, I would not succeed.

Tijana Milićević

Захвалница

На самом почетку, желим да изразим велику захвалност мојим менторима, Александру Поповићу и Мири Аничић Урошевић, за научно и стручно вођење и одличну атмосферу коју су ми обезбедили током истраживачког рада у оквиру докторских студија. Захваљујем им се на указаном поверењу и подршци и на томе што су били ментори какве сваки студент може само пожелети.

Иако Дубравка Релић није званично ментор у овој комисији, дефинитивно је то била у последње четири године док сам радила на својој докторској дисертацији. Желела бих да јој се захвалим на свим драгоценим саветима, смерницама и мишљењима, али и на подршци и охрабривању током свих ових година.

Желела бих да се захвалим и другим члановима комисије за одбрану, Гордани Вуковић, за веома корисне коментаре и сугестије приликом писања објављених научних радова и дисертације; Руланду Самсону (Roeland Samson), који ми је дао први увид у мерење магнетних параметара и омогућио ми да савладам технике магнетних мерења боравећи у његовој лабораторији; Владимиру Бешкоском за допринос у раду Комисије.

Желела бих да се захвалим винаријама „Александровић“, „Плавинци“ и „Огледном добру Радмиловац“ што су ми омогућили да спроводим експерименте у њиховим виноградима. Посебно се захваљујем Влади Јуричићу, експерту из области виноградарства који ми је дао веома корисне професионалне смјернице за организовање експерименталне поставке на терену. Такође, захваљујем се Бранislаву (власнику органске винарије), радницима из винарије „Александровић“ и Мирославу за техничку подршку приликом експерименталне поставке и сакупљања узорака.

Посебно се захваљујем Сандри Шкривањ са Хемијског факултета, Јовани Орлић из Иновационог центра Хемијског факултета и Драгица Николић са Института за хигијену и технологију меса за подршку и помоћ током хемијских анализа узорака. Захваљујем се члановима лабораторије професора Руланда (Roeland) за све смернице и савете током боравка у његовој лабораторији (посебно Ани). Поред тога, изразила бих велику захвалност господину Франку (*Rylant Frank*) из ERASMUS канцеларије и Милораду Милошевићу са Универзитета у Антверпу, за подршку у реализацији мог професионалног боравка у Белгији кроз програм ERASMUS+. Захваљујем се и Зорану Мијићу на корисним коментарима на финалну верзију дисертације.

На крају, ову докторску дисертацију посвећујем својој породици и захваљујем им се на подршци, стрпљењу и разумевању током мог школовања. Без њихове подршке не бих успела.

Тијана Милићевић

An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil−plant−air system: bioavailability and biomonitoring

Abstract

Monitoring of potentially toxic elements (PTEs) and magnetic particles in agricultural soil represents the first measure of caution regarding food safety while an investigation of element mobility and bioavailability should be a step forward in understanding the element transportation chain. In this doctoral dissertation, six experiments were performed in the different grapevine growing areas in Serbia (experimental, commercial and organic vineyards) to investigate the element mobility and bioavailability in soil−plant−air system, accompanied by an assessment of the environmental implications and human health risk, while the plant (leaves) and moss materials were tested as potential biomonitors of air pollutants in the vineyard ambients. Various single extraction procedures (deionised H_2O for 2 h and 16 h, $CaCl_2$, $BaCl_2$, NH_4NO_3, $NaNO_3$, Na_2EDTA, CH_3COOH) and pseudo-total digestion were applied to determine the element mobility and bioavailability from the soil. The PTE concentrations were measured in the soil, plant and moss samples by inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) techniques. Magnetic susceptibility (χ) was measured using magnetic susceptibility-meter, while saturation isothermal remanent magnetisation (SIRM) of magnetised samples was measured by the magnetometer.

Experiment 1 was conducted in the experimental vineyard during harvest. The bioavailability of PTEs (macro and trace elements) from soil to different grapevine parts was assessed. The non-conventional single extraction procedure using deionised H_2O during 16 h showed itself as a suitable procedure for assessing the bioavailability of trace elements. According to the environmental implication assessment, the most polluted vineyard parcel was recognised. The leaves of some grapevine varieties showed the ability to accumulate some PTEs from the soil (*Riesling rain, Riesling italian, Cabernet sauvignon* and *Cabernet franc* accumulated Zn and *Riesling rain,*

Burgundy and *Riesling italian* accumulated Cu). In addition, the skin of variety *Prokupac* markedly accumulated Ni from the soil.

Experiments 2, 3 and 4 were conducted in the commercial vineyard. In Experiment 2, bioavailability of each measured PTE was examined in the soil–grapevine system, accompanied by an assessment of the environmental implications and human health risk (assessed for field workers and grape and wine consumers). Contamination Factor (CF) implied moderate soil pollution ($1<CF<3$). The most suitable extractants for assessing element bioavailability were: $CaCl_2$, NH_4NO_3 and Na_2EDTA, while deionised H_2O could be appropriate, as well. The most bioavailable element in the soil–grapevine system was Ba. Observing biological accumulation concentration (BAC), the grape seeds and leaves mostly accumulated Cu and Zn from the soil, respectively. Influence of air deposition on the air-exposed grapevine parts, leaves and grape skin, was assessed by Ratio Factor ($RF>1$). Nevertheless, low adverse health risk effects ($HI<1$; $R\leq 1\times 10^{-6}$) were estimated for workers and consumers.

In experiment 3 soil and leaves were collected through the entire grapevine season in order to observe temporal variability of the PTE influence in the vineyard ambient. Notable environmental implications of As, B, Cd, Co, Cr, Cu, Mn, Ni and Sr to the soil were estimated. The most bioavailable PTEs from the soil to leaves were: Mn, Ni and Sr, followed by Cr and Cu, while Cd and Co were strongly bonded in the soil. Higher BAC of Al, Cd, Cu, Fe, Ni and V (in leaf set phase) and B, Cu and Zn (flowering phase) in the leaves were observed. These elements probably originated from the agrochemical applications. In veraison phase, As, Co, Cr, Mn, Pb and Sb were mostly accumulated in the leaves, and these elements could be associated with the anthropogenic sources, while Ba, Ca, Mg and Sr were mostly accumulated in the leaves collected in the harvest phase probably because of decreasing grapevine agrochemical treatments.

In experiment 4 the moss (*Sphagnum girgensohnii* and *Hypnum cupressiforme*) bags were exposed along parcels to investigate the air pollution by PTEs in the vineyard ambient and the appropriate period for the PTEs enrichment in two moss species was tested. The PTEs were significantly enriched in the moss bags after 2-month exposure and enrichment were gradually increasing up to six months. The 6-month moss exposure period could be recommended for comparative studies among different

vineyards because it could reflect the air pollution during the entire grapevine season. Both moss species reflected the spatio-temporal changes of PTE concentrations. Finally, the PTE concentrations in moss bags suggested that vineyard could represent a dominant diffuse pollution source of As, Cr, Cu, Ni, Fe and V. The significant correlations between the PTE concentrations in the grapevine leaves and in the moss bags imply that the leaves (*Cabernet sauvignon* and *Sauvignon blanc*) could also indicate Co, Cr and Ni air pollution in the vineyard.

In Experiment 5 conducted the organic vineyard, the environmental implications showed that soil was not contaminated and the grapes grown in the organic vineyard (*Panonia* and *Regent*) were safe for the consumption. The concentrations of PTEs in the organic grapevines were lower than in the studied varieties in previous experiments. However, the airborne Al, Cr, Cu, Ni and Pb deposition have an influence on the leaf and grape skin (RF>1). In addition, the moss bag biomonitors showed lower PTE accumulations in the organic than in the commercial vineyard.

In Experiment 6, both measured magnetic parameters (SIRM and χ) indicated pollution in the soil, but more suitable parameter for assessing the magnetic particles on the leaves was SIRM.

The results of this doctoral dissertation contribute to better understanding of the PTE behaviour in the soil−plant−air system and to more representative selection of single extraction procedure for PTE bioavailability assessment in the vineyard ambient. In addition, it enhances the methodology aspects of moss bag technique application, regarding exposure time, in the agricultural area, conducted for the first time in the vineyard area. Environmental risk assessments pointed out the most polluted locations in the vineyards and showed the final product (grape and wine) as safe for consumption. The cost-effective and user-friendly techniques (WD-XRF, magnetic measurements − SIRM, susceptibility) could be recommended as appropriate for detecting the pollution hot spot in the vineyards.

Keywords: vineyard, soil, grapevine parts, moss bag biomonitoring, potentially toxic elements, magnetic particles, mobility, bioavailability, environmental implication indices, health risk assessment.

Major scientific field: Chemistry
Specific scientific field: Environmental chemistry
UDC number: 504

The doctoral dissertation: “An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil−plant−air system: bioavailability and biomonitoring” was realised in the Environmental Physics Laboratory, Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade and at the Department of Applied Chemistry, University of Belgrade, Faculty of Chemistry, and in the frame of the projects:

- “Investigation of climate change and its influences on environment – monitoring the influences, adaptations, and offsets”, subproject: “An integral research of air quality in urban areas”, No. III43007, Ministry of Education, Science and Technological Development of the Republic of Serbia;
- “The study of physicochemical and biochemical processes in living environment that have impacts on pollution and investigation of possibilities for consequences minimizing”, No. 172001, Ministry of Education, Science and Technological Development of the Republic of Serbia;
- “Neutron activation analysis of environmental samples and new materials”, the bilateral cooperation between Ministry of Education, Science and Technological Development, Serbia and Joint Institute for Nuclear Research, Dubna, Russia;
- collaboration and support by the national vineries “Aleksandrović”, “Plavinci” and “Radmilovac”;
- ERASMUS+ programme for student exchange supported by the European Commission.

Based on the results and conclusions presented in this doctoral dissertation four scientific papers were published and one paper is submitted for the publication in the international journals:

1. **Milićević, T.,** Relić, D., Škrivanj, S., Tešić, Ž., Popović, A. 2017a. Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion. Chemosphere 171, 284–293.
2. **Milićević, T.,** Aničić Urošević, M., Vuković, G., Škrivanj, S., Relić, D., Frontasyeva, M.V., Popović, A. 2017b. Assessment of species-specific and temporal variations of

major, trace and rare earth elements in vineyard ambient using moss bags. Ecotoxicol. Environ. Saf. 144, 208–215.

3. **Milićević, T.,** Aničić Urošević, M., Relić, D., Vuković, G., Škrivanj, S., Popović, A. 2018a. Bioavailability of PTE in soil-grapevine (leaf, skin, pulp and seed) system and environmental and health risk assessment. Sci. Total Environ. 626, 528–545.

4. **Milićević, T.,** Relić, D., Aničić Urošević, M., Vuković, G., Škrivanj, S., Samson, R., Popović, A. 2018b. Integrated approach to environmental pollution investigation – spatial and temporal patterns of potentially toxic elements and magnetic particles in vineyard through the entire grapevine season. Ecotoxicol. Environ. Saf. 163, 245–254.

Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг

Резиме

Праћење садржаја потенцијално токсичних елемената (ПТЕ) и магнетних честица у пољопривредном земљишту представља прву меру у постизању безбедности хране, док је истраживање мобилности и биодоступности елемената веома значајно у разумевању њиховог транспорта и дистрибуције. У оквиру израде ове докторске дисертације спроведено је шест експеримената у виноградима узгајаним на различитим принципима (огледно добро, комерцијални и органски виноград) како би се испитала мобилност и биодоступност елемената у систему земљиште−биљка−ваздух. За испитивање мобилности и биодоступности елемената из земљишта примењене су различите тзв. екстракције у једном кораку (дејонизована H_2O током 2 h и 16 h, $CaCl_2$, $BaCl_2$, NH_4NO_3, $NaNO_3$, Na_2EDTA, CH_3COOH) и псеудо-укупна дигестија узорака. Биљни материјал винограда (листови) и маховине су тестирани као потенцијални биомонитори загађујућих супстанци у ваздуху у винограду. Такође, процењени су ризик за животну средину и здравље људи. Концентрације ПТЕ у узорцима земљишта, деловима винове лозе и маховинама су измерене техникама индуковано спрегнуте плазме са оптичком емисионом спектрометријом (ICP-OES), индуковано спрегнуте плазме са масеном спектрометријом и таласно-дисперзивном рендгенско флуоресцентном спектроскопијом (WD-XRF). Магнетна осетљивот (*magnetic susceptibility* − χ) и заостала магнетизација (*saturation isothermal remanent magnetisation* − SIRM) узорака земљишта и листова су измерене специфичним магнетометрима.

Експеримент 1 је спроведен у огледном добру током бербе грожђа. Процењена је биодоступност ПТЕ (макроелемената и елемената у траговима) из земљишта до различитих делове винове лозе. Неконвенционална екстракција у једном кораку коришћењем дејонизоване H_2O током 16 h се показала као погодна процедура за процену биодоступности елемената у траговима из земљишта. Применом различитих индекса за процену ризика за животну средину, идентификована је најзагађенија парцела у винограду. Листови сорти *Рајнски*

ризлинг, Италијански ризлинг, Каберне совињон и *Каберне фран* су показали способност да акумулирају Zn, а *Рајнски ризлинг, Бургундац* и *Италијански ризлинг* Cu из земљишта. Кожица грожђа сорте *Прокупац* је значајно акумулирала Ni из земљишта.

Експерименти 2, 3 и 4 су спроведени у комерцијалном винограду. У Експерименту 2 је испитивана биодоступност ПТЕ у систему земљиште–винова лоза, уз процену ризика за животну средину и здравље људи (за раднике у винограду и конзументе грожђа и вина). Фактор загађења (*Contamination Factor, CF*) показује да је земљиште у винограду умерено загађено ($1<CF<3$). Као најпогоднije екстракционе процедуре за процену биодоступности показале су се екстракције са $CaCl_2$, NH_4NO_3 и Na_2EDTA, али се и дејонизована H_2O показала као погодно средство. Баријум се показао као највише биодоступан елемент у систему земљиште–винова лоза. Према биолошкој акумулационој концентрацији (*Biological Accumulation Concentration, BAC*), семе је највише акумулирало Cu док је лист винове лозе највише акумулирао Zn. Утицај атмосферске депозиције на спољашње делове винове лозе (лист и кожицу грожђа) је процењен на основу фактора односа (*Ratio Factor, RF*) ($RF>1$). Процењен је низак ризик по здравље радника и конзумената ($HI<1$; $R\leq1\times10^{-6}$).

У Експерименту 3 узорци земљишта и листова сакупљени су током читаве виноградарске сезоне са циљем да се испитају временске варијације утицаја ПТЕ у амбијенту винограда. Примећене су веће *BAC* вредности за Al, Cd, Cu, Fe, Ni и V у периоду развоја листа и B, Cu и Zn у периоду цветања винове лозе. Присуство ових елементи је вероватно последица учестале примене пестицида у споменутим фазама развоја винове лозе. У фази шарка, елементи су који су карактеристични за антропогене изворе загађења: As, Co, Cr, Mn, Pb и Sb су се највише акумулирали у листовима, а Ba, Ca, Mg и Sr су се највише акумулирали у листовима током периода бербе грожђа што указује на смањење третмана винове лозе агрохемикалијама.

У експерименту 4, маховине *Sphagnum girgensohnii* и *Hypnum cupressiforme*, су у врећицама изложене у парцелама ради испитивања загађења ваздуха ПТЕ у винограду. Истовремено је и тестиран одговарајући период акумулације ПТЕ у две врсте изложених маховина. ПТЕ су се значајно

акумулирали у маховинама након 2 месеца излагања, али се акумулација постепено повећавала са продужавањем периода излагања маховина са 2, преко 4 до 6 месеци. Период од 6 месеци излагања може се препоручити за упоредне студије између различитих винограда јер одражава загађење ваздуха током целе виноградарске сезоне. Обе врсте маховина одражавале су просторно-временске промене концентрација. На крају, концентрације ПТЕ у маховинама указују да виноград може представљати доминантни дифузни извор загађења As, Cr, Cu, Ni, Fe и V. Статистички значајне корелације између концентрација Co, Cr и Ni у листовима винове лозе и у маховинама указују да листови сорти *Каберне совињон* и *Совињон блан* могу такође индиковати загађење вадуха у винограду.

Експеримент 5 је спроведен у органском винограду. Индекси за процену ризика за животну средину су показали да земљиште није контаминирано и да је грожђе које се узгаја у органском винограду (*Панонија и Регент*) безбедно за конзумирање. Концентрације ПТЕ у органски узгајаној виновој лози су биле ниже од концентрација у испитиваним сортама у претходним експериментима. Међутим, Al, Cr, Cu, Ni и Pb се такође могу суспендовати из ваздуха на лист и кожицу грожђа (RF>1). Поред тога, маховине у врећицама као биомонитори су акумулирале ниже концентрације ПТЕ у органском него у комерцијалном винограду.

У Експерименту 6, оба измерена магнетна параметра (SIRM и χ) су индиковала загађење земљишта у винограду, док се за индикацију загађења листова магнетним честицама као погодинији може истаћи SIRM.

Резултати ове докторске дисертације доприносе бољем разумевању понашања елемента у систему земљиште−биљка−ваздух и доприносе репрезентативнијем избору екстракција у једном кораку за процену биодоступности ПТЕ у виноградима. Поред тога, добијени резултати унапређују постојећу методологију примене технике маховина у врећицама у пољопривредној средини, у погледу дужине периода излагања. Процене ризика по животну средину и здравље људи указују на потенцијално загађење испитиваних локација и на то да ли је крајњи производ (грожђе и вино) безбедан за употребу. Једноставније и економичније технике (WD-XRF, магнетна мерења) могу бити

препоручене као прикладне за индикативно проналажење интензивнијег загађења у виноградима.

Кључне речи: виноград, земљиште, делови винове лозе, активни бимониторинг, потенцијално токсични елементи, магнетне честице, мобилност, биодоступност, индекси за процену еколошког ризика, ризик по људско здравље.

Научна област: Хемија
Ужа научна област: Хемија животне средине
УДК: 504

Докторска дисертација „Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг“ рађена је у оквиру пројеката:

- „Истраживање климатских промена и њиховог утицаја на животну средину – праћење утицаја, адаптација и ублажавање“, бр. ИИИ43007, област интегралних интердисциплинарних научних истраживања финансиран од стране Министарства просвете, науке и технолошког развоја Републике Србије;
- „Проучавање физичкохемијских и биохемијских процеса у животној средини који утичу на загађење и истраживање могућности за минимизирање последица“ бр. No. 172001 финансиран од стране Министарства просвете, науке и технолошког развоја Републике Србије;
- „Neutron activation analysis of environmental samples and new materials„ билатерална сарадња Министарства просвете, науке и технолошког развоја Републике Србије са Обједињеним институтом за нуклеарна истраживањаbilateralna saradnja sa (JINR), Дубна, Русија;
- сарадње и подршке винарија „Александровић“, „Плавинци“ и „Радмиловац“;
- ERASMUS+ програма за студентску размену подржаног од стане Европске Комисије.

На основу резултата и закључака презентованих у овој докторској дисертацији објављени су следећи радови у међународним часописима (један у међународном часопису изузетних вредности M21a и три у врхунским међународним часописима M21):

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

2. **Milićević, T.,** Aničić Urošević, M., Vuković, G., Škrivanj, S., Relić, D., Frontasyeva, M.V., Popović, A. 2017b. Assessment of species-specific and temporal variations of major, trace and rare earth elements in vineyard ambient using moss bags. Ecotoxicol. Environ. Saf. 144, 208–215.

3. **Milićević, T.,** Aničić Urošević, M., Relić, D., Vuković, G., Škrivanj, S., Popović, A. 2018a. Bioavailability of PTE in soil-grapevine (leaf, skin, pulp and seed) system and environmental and health risk assessment. Sci. Total Environ. 626, 528–545.

4. **Milićević, T.,** Relić, D., Aničić Urošević, M., Vuković, G., Škrivanj, S., Samson, R., Popović, A. 2018b. Integrated approach to environmental pollution investigation – spatial and temporal patterns of potentially toxic elements and magnetic particles in vineyard through the entire grapevine season. Ecotoxicol. Environ. Saf. 163, 245–254.

Content

1 Introduction

The agricultural practice represents one of the significant environmental pollution sources beside industry and traffic activities (WHO, 2018), but also different anthropogenic sources of pollution have the influence on the agricultural soil, plant growth, field worker health and finally grape consumer health. The increasing release of agrochemicals into the environment has led to growing public concern over the potential higher accumulation of pollutants including potentially toxic elements−PTEs; rare earth elements−REEs and particles with magnetic properties−magnetic PM in agricultural soil and consequently in the plants. Viticulture represents an important agricultural practice in many countries and long-term use of diverse inorganic (metal-based) and organic pesticides and fertilisers poses serious environmental threats (Komárek et al., 2010). Since the agrochemicals' utilisation is growing worldwide (US EPA, 2012), exposure to this group of emerging pollutants, has also raised questions about their detrimental health effects (Pagano et al., 2015). Nowadays, organic viticulture production becomes more and more popular because of a lack of detrimental effects on the environment and human health in comparison to conventional production (Häring et al., 2001). Organic grapevine and wine production are now present in almost all of Europe, following the years the regulations in this field were changing and improving, and finally, the valid rules (by Standing Committee on Organic Farming−SCOF) was approved 2012 (European Commission, 2012). In Serbia, the Law on organic production is involved in the national regulations (Official Gazette of Republic Serbia, 2010).

In the vineyard soils, a serious impact on the soil pollution could be caused by the pollutants coming from the fertilisers and pesticides (Kabata–Pendias and Mukherjee, 2007), but also from some other surrounding or remote sources such as industrial activities or traffic. Monitoring of pollutant concentrations in agricultural soil represents the first measure of caution regarding food safety, while the research of the pollutant mobility and bioavailability in the soil−plant−air system should be a step forward in understanding the element uptake and translocation in the plant and it could substantially improve the regulatory control of the agricultural production of fruits and vegetables. The elements in soil may adversely affect human health through the inhalation of dust, ingestion of soil or by dermal contact (Morel, 1997; Sylvain et al., 2016). Moreover, the increased concentration of PTEs in soils can cause a potential risk

to human health because of their subsequent involvement in the food chain by plant uptake (Radha et al., 1997; Islam et al., 2015; Niesiobędzka, 2016). According to the available literature, more than one single extraction procedures were applied only in a few studies for assessing the mobility or bioavailability of PTEs in the soil-plant system specifically in the vineyards that furthermore could be useful to assess environmental or health risk assessment (Rao et al., 2010; Vystavna et al., 2014; Vázquez Vázquez et al., 2016), which is one of the experimental aims presented herein. The studied extraction procedures (deionised H_2O, weak salt solutions: $CaCl_2$, $BaCl_2$, NH_4NO_3 and $NaNO_3$, complexing agent Na_2EDTA and weak acid CH_3COOH) are a simple-performing and cost-effective way to assess the labile element fractions in soils (Beckett, 1989; Gupta, 1996; Paterson et al., 1996; Ure, 1996; Meers et al., 2007; Rao et al., 2008; Poggio et al., 2009; Santos et al., 2010).

The monitoring of the air pollution in agricultural areas is often being neglected. Air pollution is not only a local, but it is also a regional and global issue since air pollutants released from one source may be transported in the atmosphere, contributing to or resulting in poor air quality elsewhere (EEA, 2016). The regulatory monitoring of air pollution by devices usually requires electricity supply, permanent maintenance of the equipment and their installations in the agricultural areas would be quite expensive. The plant material naturally present or growth in the agricultural areas can be used as a passive biomonitor. Hence, moss biomonitoring represents a complementary cost-effective approach to the regulatory air pollution measurements. Specifically, the active moss biomonitoring of trace elements could be performed in agricultural regions, which has been rarely reported thus far (Capozzi et al., 2016a; 2016b). The recommended variables regarding the application of the method in urban and industrial areas – preparation of the moss and transplants, exposure and post-exposure treatment (Ares et al., 2012) should be further tested for the agricultural ambient.

This doctoral dissertation represents an extension to the candidate's master work entitled "*Poređenje različitih tipova ekstrakcionih sredstava za izolovanje elemenata koji su lakodostupni biljkama*" (in Serbian). The main aims of this doctoral dissertation were to move forward into the investigation of the PTE mobility and bioavailability in the soil−plant−air system in the vineyard ambients. The doctoral dissertation is

organised as a review of the published scientific manuscripts and some additional unpublished material. The main aims were to:

- assess which of the single extraction procedures are the most suitable for assessing the PTE mobility and bioavailability contributing to the better understanding of the PTE behaviour in the soil−plant−air system;
- compare the application of various ecological implication indices for assessing the pollution influences in different vineyard ambients (experimental, commercial and organic vineyards), to assess seasonal environmental influences and origin and behaviour in the soil−plant−air system;
- assess air pollution in agricultural (vineyards) ambient applying the moss bag biomonitoring technique, and make a new insight into the methodology of moss bag biomonitoring in the vineyard ambient;
- test the grapevine leaves as potential air/ambient pollution biomonitors;
- assess which of the studied vineyards is less exposed to pollution?
- test non-destructive and user-friendly techniques (WD-XRF and magnetic measurements) for the assessment of PTEs and magnetic PM pollution in vineyard ambient;
- assess the health risk for workers in the fields and grapevine (and wine) consumers.

2 Theoretical background

2.1 Agricultural areas and environmental pollution

One of the most serious problems facing humanity and other living organisms on Earth is environmental pollution. It is defined as "the contamination of the Earth's components to such an extent that normal environmental processes are adversely affected" (Muralikrishna and Manickam, 2017). Rapid urbanisation, industrialisation and commercialisation of the undeveloped areas seriously affect the environmental quality. Environmental pollution poses a global problem with diverse and substantial public health implications. Pollutants can be naturally occurring substances in the environment, but present in excess of natural levels they can cause serious environmental pollution. Any natural resources exploitation more than those which can be restored itself results in the pollution of air, water or soil (Muralikrishna and Manickam, 2017). The agricultural areas are recognised as one of the most significant environmental pollution sources together with industry and traffic (WHO, 2018), but on the other hand, the other anthropogenic pollution sources could affect the agricultural areas, soil, cultivated plants, workers' health and further the food chain and consumers' health. According to the Food and Agriculture Organisation of the United Nations (UN FAO), agricultural land covers 38.4% of the world land area (FAOSTAT, 2018). Specifically, pastures cover 68.4% (26.3% of global land area), arable land (row crops) covers 28.4% (10.9% of global land area), and crops (e.g. vineyards and orchards) cover 3.1% (1.2% of global land area) of total agricultural land.

Agricultural areas distinguish from the non-cultivated areas by the excessive and frequent application of agrochemicals for improving crop growth. Agrochemicals significantly contribute to elevating pollutants' concentrations in the agricultural environment (soil, plants and air) which further threatening human health through the food chain. Contamination by PM, PTEs and REEs together with erosion and other geogenic processes, have a negative influence on the soil quality and poses high environmental and health risk threats. The grapevine growing areas represent intensively treated agricultural areas by the agrochemicals. Viticulture is one of the most important agricultural practices in many countries worldwide and the frequent application of the agrochemicals leads to increasing different pollutant concentrations in soils–plant–air system in the vineyards (Flores-Vélez et al., 1996; Ribolzi et al., 2002;

Hildebrandt et al., 2008; Komárek et al. 2010). However, the intensive and frequent agrochemicals application in vineyards is of public concern, because of the presence of agrochemical residues in grapes, wine and groundwater and their influence to the workers and consumers health (Jacobson et al., 2005; Komárek et al. 2010).

The grapevine growing is increasing in the Republic of Serbia what is important it contributes to the affirmation of rural areas and the promotion of the wine producing areas (Figure 2.1).

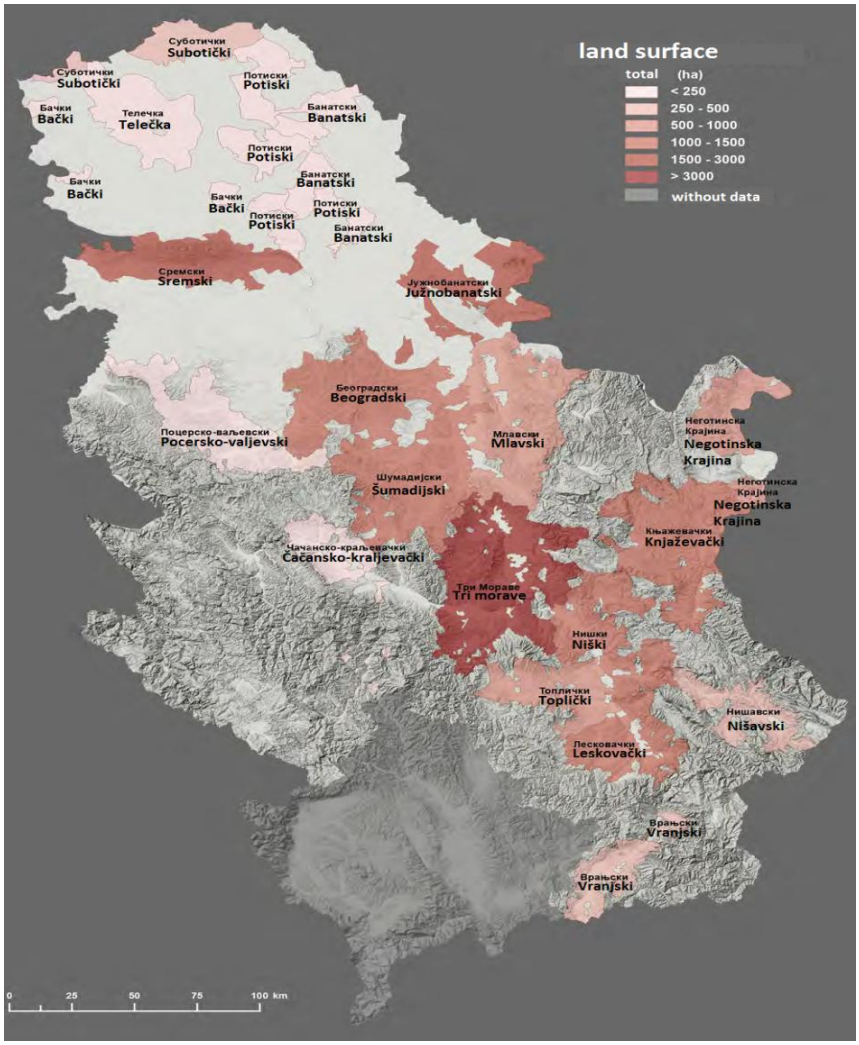


Figure 2.1 Lend surface of Republic of Serbia covered by the vineyards among the vineyard regions and subregions (adopted and modify from Ivanišević et al., 2015).

In Serbia, grape production per year is 145 829 t (FAOSTAT, 2018). In the territory of Serbia, there are three vineyard regions (Central Serbia region, a region of

Vojvodina and region of Kosovo and Metohija). In these three regions, there are 22 subregions and 77 vineyards. In this doctoral dissertation, three different vineyards were investigated (two conventionally growth – experimental and commercial and one organically growth). These vineyards are located in the Central Serbia region, where the vineyards cover 17 118 ha of the land surface (Figure 2.1). The experimental and the organic vineyards are located in the Belgrade subregion and the commercial one is located in the Šumadija subregion (Figure 2.1) (Ivanišević et al., 2015).

2.1.1 Particulate matter

Particulate matter (PM) is the term which is used for a multi-phase mixture of solid particles and liquid droplets from the air. World Health Organization (WHO) promotes PM as the most serious and harmful than any other air pollutants (WHO, 2016). Various epidemiological studies have shown significant correlations between airborne PM pollution and respiratory and cardiovascular diseases and also lung cancer and ultimately death (Marcazzan et al., 2001; Pope et al., 2002; Knutsen et al., 2004; Knox, 2006). PM can be emitted from vehicles, power plant smokestacks, construction sites, unpaved roads, fields, different industries, or as the products of complex reactions of directly emitted chemicals. The major PM constituents are sulphate, nitrate, ammonium, chloride, elemental carbon, organic carbon, crustal materials (soil dust and wind-blown particles) and biological materials (pollens, spores and plant pieces), PTEs, RREs (Harrison and Yin, 2000) and PM can also contain the magnetic minerals such as Fe-oxides. These coarse PM mostly originates from crustal materials (soil and dust) or originating from the sea salts or biological materials (Nel, 2005; Pope and Deckery, 2006), while fine PM mainly originates from the combustion of the fossil fuels. The proportion of components varies considerably based on the sampling location; e.g. crustal materials and more common in dryer climates (Harrison and Yin, 2000). Pollutants, such as metals, organic compounds and reactive gases, can be absorbed to and transferred by PM (Kampa and Castanas, 2008). Metals, such as Cd, Cr, Co, Cu, Fe, Hg, Ni, V and Zn are important for particle toxicity and can be toxic at very low concentrations (Schwarze et al., 2006).

Particles exist in many different shapes and sizes (Figure 2.2) and they can be constituted of many different organic and inorganic chemicals (pollutants). One of the

first pollutants regulated by the European Union (EU) legislation were PM10 and PM2.5 (particles of 10 and 2.5 μm in diameter, respectively) and some associated toxic elements (As, Cr, Hg, Ni and Pb) (Kuklinska et al., 2015), prescribed in 1979, by the Convention on Long-range Transboundary Air Pollution (CLRTAP). The PM with diameter <10 μm (PM10) can deeply penetrate into the lungs causing serious respiratory and cardiovascular illness depending on the PM-associated pollutants (Kelly and Fussell, 2012).

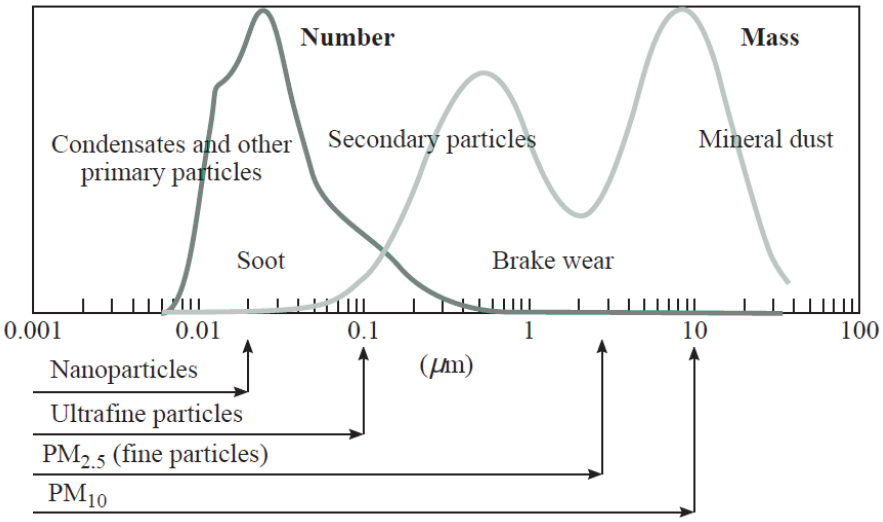


Figure 2.2 Distribution of numbers and masses versus size of airborne particles; from vehicular traffic particles origin is marked (condensates, soot and brake-wear) from road abrasion, agricultural and natural sources the mineral dust are marked (adopted and modify from Biard and Cann, 2012).

2.1.1.1 Magnetic particulate matters

Magnetic minerals are present primarily in the soil parent material, i.e. PM with magnetic properties from the air can be deposed, weathered, transported or subjected to chemical and thermal transformations (Thompson and Oldfield, 1986; Verosub and Roberts, 1995; Evans and Heller, 2003). Thus, they are present in the environment with different associations which are based on their source and formation (Maher et al., 2008). Magnetic minerals can be transported between the different Earth spheres like other air pollutants (Urbat et al., 2004). Different anthropogenic but also natural sources produce PM, which have specific magnetic properties. Anthropogenically originated PM (e.g. from fly-ashes, industrial smelters, coal-burning activities) are enriched by the toxic elements (Petrovský and Ellwood, 1999). The elements are usually incorporated

into crystal lattices or can be absorbed on magnetic mineral surfaces, especially iron-oxides (Petrovský et al., 2000; Mishra and Tripathi, 2008; Salo, 2017). Thus, measuring the magnetic parameters of deposited atmospheric particles can serve as an alternative parameter in assessing the pollution in different environmental ambients. Thus, the determination of magnetic parameters is based on the assumption that atmospheric PM contain significant ferro(i)magnetic iron oxides and sulfides enriched with PTEs. As it was confirmed by e.g. Hunt et al. (1984), Petrovský et al. (2013) and Muxworthy et al. (2003) who have found significant correlations between PTE concentrations in atmospheric PM and their ferro(i)magnetic fraction. In PM, the PTE concentrations mostly depend on polluting source and the distance of the pollution source (Hofman et al., 2017).

2.1.1.1.1 Magnetic parameters as a proxy of magnetic PM

The presence of magnetic domains in materials with ferromagnetic and ferrimagnetic properties, in the alternating magnetic field, cause magnetisation. The magnetic response of a material to magnetic field sweeping − H is defined by magnetic hysteresis (magnetisation−M) (Figure 2.3). The hysteresis loop can be interpreted as a magnetic mineralogical signature, where the loop height shows a function of the type of magnetic minerals, concentration, and the width of loop shows the magnetic "hardness" of the sample so-called coercivity−HC, influenced by mineralogy and grain size of the material. Due to the defined properties (Figure 2.3): saturation magnetisation−MS, saturation remanent magnetisation−MRS, coercivity−HC, and the remanence coercivity−HCR, the loop shape of hysteresis usually reduces. When the sample is exposed to a large saturating manetisation−MS, magnetisation remaining after removal of the saturating field is MRS (H=0), the negative field which is necessary for sample magnetisation reduce to zero is HC (Figure 2.3), and the negative field which is necessary for reducing the remanent magnetisation to zero is HCR (HCR>HC). MRS can also be named as saturation isothermal remanent magnetisation (SIRM). MS represents a measure of magnetic concentration, while SIRM represents a proxy also for the concentration, but it also depends on the mineralogy and grain size (Hofman et al., 2017; Salo, 2017). Independents of the concentration are HC and HCR which are controlled by mineralogy and grain size (Hofman et al, 2017). A remanence obtained by

exposure to the magnetic field at room temperature represents the remanent magnetisation (IRM). This may appear in the environment (e.g. in strike lightning) but often this is related to the experimental procedures performed in the laboratory when the investigated sample is exposed to the known magnetic field. If the magnetic field used to provide IRM enough to achieve saturation, the magnetisation is called isothermal remanence (SIRM) (Figure 2.3). However, the term SIRM is often applied to show the remanence obtained by the investigated sample after exposure to the highest available magnetic field (usually 1 T) (Michael and Friedrich, 2003).

The gradient of the response of the magnetisation (M) to the magnetic field (H), which is determined by hysteresis curve slope, and it is named volume magnetic susceptibility (χ, dimensionless). It can be determined for high frequency (χHF) or low frequency (χLF) fields (Figure 2.3) (Hofman et al, 2017). The χ value depends on the magnetic mineralogy, concentration (Salo, 2017).

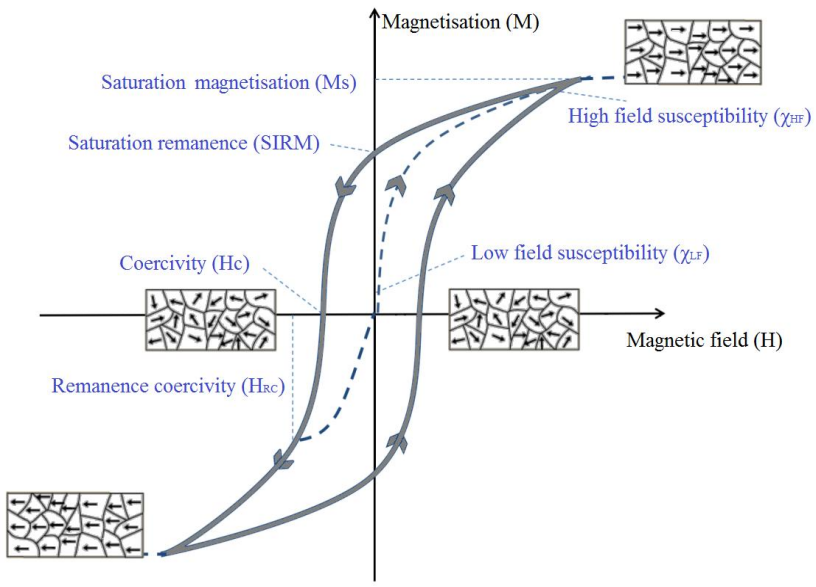


Figure 2.3 Ferromagnetic material magnetic hysteresis (M-H) loop and magnetic properties most usually applied in the studies of magnetic measurements; The susceptibility (low and high field − shown by the M-H curve slope); initial magnetisation (dashed line in upper right quadrant on the graph) and the samples' magnetic remanence at remanence coercivity (lower left quadrant) (adopted and modify from Hofman et al, 2017).

2.1.2 Potentially toxic elements

Observing the literature, in the various environmental studies the chemical elements are referred as different terms (major and minor elements, trace elements,

major and trace elements, toxic elements, heavy metals, etc.). Although none of the terms is entirely satisfactory from a chemical point of view and in the past "heavy metals" was the most popular term used in the literature and widely recognised for large element group, but neither all elements are metals or "heavy". In addition, the term "toxic metals" is also not appropriate since elements become toxic to environment and living organisms only when they are present in excess levels. The elements present in excess in the environment (soil, plants, air etc.) could cause the environmental and health risk implications. For this reasons, in environmental studies, chemical elements are also often referred to as potentially toxic. Likewise, this term is more inclusive and appropriate than "toxic elements" or "heavy metals" (Hooda, 2010; Kabata-Pendias and Kabata, 2001). Hence, in this doctoral dissertation, they will be named as PTEs, except when specific differences are investigated between major and minor chemical elements in the studied samples (where PTEs were also named as major and trace elements, Experiment 1).

The elements play an important role in each biogeochemical cycle. In various ecosystems, PTEs are enriched, while the source can be either natural (lithogenic or geogenic) or anthropogenic (caused by humans). Some natural processes in the environment such as mineral weathering (erosion and deposition of wind-blown particles), volcanic eruptions, soil erosion, forest fires or biogenic sources are releasing PTEs into the biosphere (Nogawa, 1981; Sakamoto et al., 2001; Tack, 2010). While PTEs originating from natural sources constitute a significant burden of PTEs in the environment, the contribution from anthropogenic sources can be several times higher than those from the natural sources (Nogawa, 1981; Tack, 2010), adversely influencing the environment and human health. Anthropogenic sources of PTEs are related to industrial activities (mining and smelting, discharge of wastewater and air deposition from industrial fumes) and agricultural activities (application of sewage sludge, fertilisers, pesticides and erosion). Undoubtedly, the anthropogenic activities represent the major source of PTE accumulation into the biosphere especially if the pollution sources are located near investigated ambient. Worldwide, there are concerns raised about the PTEs accumulation in agricultural soils because they can easily transfer from this environment to the agricultural products and further in the food chain and finally to

humans (Rinklebe et al., 2017). The major PTE anthropogenic sources influencing environmental pollution are:

- air pollution and atmospheric deposition of the pollutants (wood, coal and gasoline combustion, metal mining, smelting, manufacturing, waste burning, production of fertilisers);
- application of sewage sludge, manure and organic wastes or co-products from agriculture and food industry in the agricultural areas;
- disposal of industrial co-products, waste, coal and wood ashes;
- fertilisers, agrochemicals (pesticides) frequent application in agricultural areas (Tack, 2010).

According to Kabata-Pendias and Pendias (2001), the most potentially toxic elements to the biosphere may be Ag, Au, Cd, Cr, Hg, Mn, Pb, Sb, Sn, Te, W and Zn. However, this list is not totally in correspondence to the list of PTEs considered to have a high risk to the environment and human health: Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V and Zn (Kabata-Pendias and Pendias, 2001). According to International Agency for Research on Cancer (IARC), some of PTEs (As, Cr, Hg, Ni and Pb) are considered as carcinogenic substances type I, while the other PTEs, depending on the quantities in the environment, could have toxic or carcinogenic effects, even some rare earth elements (REEs) (Dołęgowska and Migaszewski, 2013). The most significant anthropogenic PTE sources represent traffic emissions (Ba, Cr, Cu, Fe, Mn, Pb and Zn), fossil fuel combustion (Cd, Cr, Mn, Ni, Pb, Sb and V), metals production (Cd, Cr, Cu and Zn), gasoline combustion (Pb) (Schauer et al., 1996; Pacyna and Pacyna, 2001; Bilos et al., 2001; Ristić et al., 2013; Kabata–Pendias and Mukherjee, 2007) and agricultural practice (pesticides: As, Br, Cu, V and Zn and fertilisers: B, Ba, Be, Bi, Ca, Cd, Cr, Cu, K, Mo, Mg, Ni, P, S, Sr, Zn and REEs) (Kabata–Pendias and Mukherjee, 2007).

In the agricultural soils, which is the main sink of the PTEs originating from both anthropogenic and geogenic sources, the most significant PTE sources in the agricultural areas are originating from the frequent application of agrochemicals (pesticides, manure, fertilisers) (Table 2.1) but also PTEs could originate from some surrounding or remote pollution sources (traffic, industry, combustion activities etc). The prolonged application of mineral fertilisers and pesticides–fungicides has resulted in the Cu, Zn, Cd, Pb and As accumulation in the agricultural soil where Ni, Cr, Co and

Fe concentrations are controlled by parent material influences (Komárek et al., 2010; Kelepertzis, 2014). The concentrations of Ni, Cd, Zn, Pb, As and Cr correlate with the P concentrations suggesting that the rock phosphate is the major source of these elements (Nziguheba and Smolders, 2008; Jiao et al., 2012). The research interests have also been induced by widespread application of fertiliser containing REEs, especially in China (Wen at al., 2001).

Table 2.1 Table presenting the agricultural sources of PTEs contamination (mg kg^{-1}) in soils (adopted from Kabata-Pendias and Pendias, 2001)

	Sewage sludges	Phosphate fertilisers	Limestones	Nitrogen fertilisers	Manure	Pesticides (%)
Aa	2−26	2−1200	0.1−24	2−120	3−25	22−60
B	15−1000	5−115	10	6	0.3−0.6	
Ba	150−4000	200	120−250		270	
Be	4−13		1			
Br	20−165	3−5		6−716	16−41	20−85
Cd	2−1500	0.1−170	0.04−0.1	0.05−8.5	0.3−0.8	
Ce	20	20	12			
Co	2−260	1−12	0.4−3	5−12	0.3−24	
Cr	20−40600	66−245	10−15	3−19	5.2−55	12−50
Cu	50−3300	1−300	2−125	1−15	2−60	18−45
F	2−740	8500−38000	300	82−212	7	
Ge	1−10		0.2		19	0.8−42
Hg	0.1−55	0.01−1.2	0.05	0.3−3	0.09−0.2	
Mn	60−3900	40−2000	40−1200		30−550	
Mo	1−40	0.1−60	0.1−15	1−7	0.05−3	
Ni	16−5300	7−38	10−20	7−38	7.8−30	60
Pb	50−3000	7−225	20−1250	2−1450	6.6−15	
Rb	4−95	5	3	2	0.06	
Sb	/			2−600		
Sc	0.5−7	7−36	1		5	
Se	2−10	0.5−25	0.08−0.1		2.4	
Sn	40−700	3−19	0.5−4	1.4−16	3.8	
Sr	40−360	25−500	610	100−5420	80	
Te	/	20−23			0.2	
U	/	30−300				
V	20−400	2−1600	20			45
Zn	700−49000	50−1450	10−450	1−42	15−250	1.3−25
Zr	5−90	50	20	6−61	5.5	

2.1.2.1 Rare earth elements

Rare earth elements (REEs) represent a group of 17 elements from the periodic table: 15 lanthanides $_{57}$La, $_{58}$Ce, $_{59}$Pr, $_{60}$Nd, $_{61}$Pm, $_{62}$Sm, $_{63}$Eu, $_{64}$Gd, $_{65}$Tb, $_{66}$Dy, $_{67}$Ho, $_{68}$Er, $_{69}$Tm, $_{70}$Yb, $_{71}$Lu, together with $_{39}$Y and $_{21}$Sc. All of these elements have similar chemical properties (Loell et al., 2011; Tyler, 2004; Mihajlovic and Rinklebe, 2018). Those with lower atomic weight, from La to Sm, with atomic numbers from 57 to 62,

are referred to the light rare earth elements (LREE); while elements from Eu to Lu, with atomic numbers from 63 to 71, represent a group of heavy rare earth elements (HREE) (the grouping into LREE and HREE vary somewhat, and the term "mid-REE" can be found sometimes in the literature). Because of its chemical similarity to the alkaline earth and other rare earth elements Y, although with a lower atomic weight, is grouped with the HREE (Kabata–Pendias and Mukherjee, 2007). Scandium's chemical properties differed enough from the other REEs and sometimes it is excluded from the REE observations in the literature. Rare earth elements have similar physical and chemical properties. Generally, REEs exhibit lithophilic affinity and occur in the environment as trivalent ions. In the environment, Ce can also be present as tetravalent ion and Eu as a divalent ion (Kabata–Pendias and Mukherjee, 2007). Contrary to their name "rare", those elements are very often present in the Earth's crust. Those elements exist in minerals e.g. carbonates, silicates, fluorides, and phosphates (Laveuf and Cornu, 2009).

Increased use in high-tech industry e.g. solid-state lasers, storage media for data handling, mobile phones, photovoltaic cells, catalysers in cars, lodestones and ceramics manufacturing, caused that REEs content in the environment is increasing (Humphries, 2010). In last decades, in some countries, microelement fertiliser containing REEs are also being used in plant production (Hu et al., 2006; Pang et al., 2002; Tyler, 2004; Tyler and Olsson, 2005; Mihajlovic and Rinklebe, 2018). An increasing release of REEs may have negative impacts on the environment and further on humans. Nevertheless, the REEs mobilisation and their possible impacts on the environment are still not investigated well. Since now, these elements have been classified neither as essential nor as toxic (Tyler, 2004), thus in this thesis, they will be observed as PTEs. There are no observations of the significantly toxic effects of REEs to plants, but they have impairing effects on cell membranes of vascular plants and on the Ca metabolism in microorganisms. RREs occurring in oxide forms are apparently slightly available to both humans and animals. Other salts of REEs, however, might be easier absorbed by humans. Their danger is mainly from aerial dust inhalation by humans (Kabata–Pendias and Mukherjee, 2007).

2.2 Potentially toxic elements in the soil−plant−air system

Determination of the PTEs 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). Also, in the agricultural areas, PTEs from the air can be deposed on the surface (soil or plant). The transport, residence time, and fate of the pollutants in a particular ecosystem have been of special environmental concern. The behaviour of trace elements in each ecosystem is very complex and therefore has usually been studied separately for air, water, soil and biota. The urgent environmental problem at the present time is closely associated with pollution in which PTEs play a significant role.

2.2.1 Mobility and chemical reactions of the potentially toxic elements in the soil

The effects of PTEs present in excess in soil depend on complex reactions between the PTE cations and other soil components in all soil phases (solid, liquid and gaseous). The mobile PTE fraction in soil behaves like cations and it is controlled by dynamic equilibrium between solid and liquid soil phases. However, in the soil, all possible reactions represent the complex systems of various chemical reactions. The fate of PTEs in soils depends on different soil processes: dissolution, sorption, complexation, migration, precipitation, occlusion, diffusion (into minerals), binding by organic substances, absorption and sorption by microbiota and volatilisation (Kabata Pendias and Pendias, 2001; Hooda, 2010). All these processes in soil are conditioned by some soil properties, such as soil pH and redox potential, which are the most important physico-chemical parameters influencing the fate of PTEs and their mobility and bioavailability in soil. Thus, the solubility of PTEs is often shown as a function of pH affected by the soil organic matter (OM) content. Also, other soil physico-chemical parameters, such as CEC, carbonates content, Fe and Mn hydrated oxides, clay minerals and granulometric fractions also have a significant influence on the behaviour of PTEs

in the soil. The frequent association of the PTEs with the acid deposition (mostly from SO_2 and NO_x which further transform into acid form) has an influence on overall ecological disturbance created by the chemical reactions in soils (Kabata Pendias and Pendias, 2001).

A major total PTE content fraction is usually associated with the solid soil phase and PTEs can be superficially adsorbed or complexed with solid-phase components (clay minerals, Fe and Mn oxides or OM) and those PTEs are more or less exchangeable with the soil solution phase. Those PTEs which are structurally incorporated in the soil minerals not seem to be available. Physical, chemical and biological processes determine the speciation, redistribution, mobility and ultimately the bioavailability of PTEs in soils (Tack, 2010). The PTEs distribution between the various chemical species in soil solid or solution phase is defined as speciation (Templeton et al., 2000) and these species can be defined as (Brümmer, 1986; Tack, 2010): i) soil solution phase species including free ions, inorganic complexes, organic complexes, bound to suspended colloids (clay, OM, sesquioxides) as in the solid phase; ii) soil solid phase species including exchangeably bound to surfaces (sorption), complexed or occluded with OM, adsorbed or occluded in oxides and hydroxides of Fe, Mn and Al or carbonates, as precipitate or as structural components in minerals.

In the soil, many PTEs exist only in one dominant oxidation state, but some (e.g. As and Cr) occurs in different oxidation states (e.g. As^{3+} or As^{5+} and Cr^{3+} or Cr^{6+}), which can interact with different soil compounds that react as oxidating or reducing agents in the chemical reactions of oxidation or reduction (Brümmer, 1986; Tack, 2010). Many PTEs in soil solution exist in their most simple oxidation states (for example, Zn^{2+}, Cu^{2+}, Ni^{2+}) surrounded by six H_2O molecules in the octahedron. Some other elements (e.g. Mo) are present in the soil as oxyanions (for example MoO_4^-) (Barrow, 1999; Tack, 2010). The most toxic Cr form in the environment is Cr^{6+} which is present as $CrO4^{2-}$ in the soil solution (Tack, 2010 and references therein). Aside, B exists as H_3BO_3 in soil solution (Goldberg et al., 2000), and Pb occurs in the soil as organometallic compounds (e.g. alkyl lead compounds) (Teeling and Cypionka, 1997; Tack, 2010). The complex compounds in the soil are constituted of one or more metal cations bound to ligands. The metal acts as a Lewis acid, which is capable for accepting an electron pair and form a bond, while the ligands (ion or neutral molecule) represents

the Lewis bases and they provide a free electron pair for building a chemical bond. The cations of metals usually have a tendency to build complexes interacting with chlorides, sulfates, nitrates etc. In the soil environment, most of the elements also tend to form hydroxo-complexes (e.g. $ZnOH^{-}$) (Evans, 1989). Thus, the most significant ligand for building the complexing compounds in the soil system is OH^{-}, but for example, the carbonate complexes are the most important for Cu^{2+} occurrence in the soil, while Cl^{-} anion is significant for binding some divalent cations such as Cd^{2+}. All these complexes are usually weak and labile, and they can influence the significantly PTE behaviour in the soil. Contrary, complexes of PTEs with organic substances are usually stable, including bounding with simple organic acids (e.g. CH_3COOH), which are present in the soil solution or the soluble OM, which contains some high molecular weight compounds. Thus, the behaviour of many elements (e.g. Fe, Cu, Pb) in the soil are highly influenced by the soil OM (Tack, 2010 and references therein).

The term "sorption" includes adsorption and absorption. Adsorption is the chemical process of solute adhesion to a solid surface, whereas absorption represents the process in which the solution diffuses into a porous solid and it is attached or dissolved to inner surfaces (Fetter, 1993). The sorption of ion may be conditioned by inner sphere-complexation, outer-sphere-complexation or diffuse ion swarm, and the specific selectivity of PTEs sorption is influenced by their properties such as ionic radius, polarity, hydrated radius, equivalent conductivity, hydration enthalpy and entropy, availability sorption sites, steric factors, affinity of the ions for formation the complex and their stability and various interactions (Bradl, 2004; Tack, 2010).

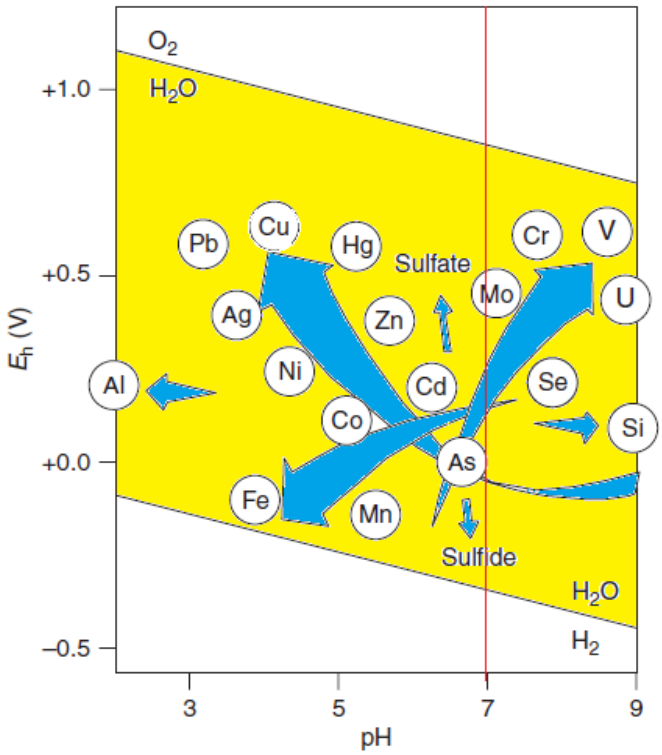


Figure 2.4 Schematic representation of major trends for increasing element mobility in soils (broadening blue arrows) as a function of redox potential and pH (adopted and modify from Tack, 2010).

The most specific physico-chemical parameters influencing all chemical processes and further the elements behaviour in soil system are pH and redox potential (Eh). The influences of these parameters on the different elements in the soil solution are presented in Figure 2.4, where decreased pH-induced the increase of H^+, Fe^{3+}, Al^{3+} activity in the soil solution. Thus, those elements tend to compete with PTEs for the sorption sites. When pH is lower than 6 in the soil solution, the PTEs mobility decreases following the order: Cd > Zn > Ni > Mn > Cu > Pb > Hg (Cottenie and Verloo, 1984; Tack, 2010). Under the pH>7, the anions of As, Mo, Se and Cr are more mobile (Figure 2.4). In addition, the presence of free $CaCO_3$ can reduce the solubility of PTEs, because it increases pH value of soil (Tack, 2010 and references therein). According to the soil pH conditions, different PTEs mobility is summarised in Table 2.2 (Kabata-Pendias and Pendias, 2001).

Table 2.2 The element mobility described by the soil conditions (adopted from Kabata-Pendias and Pendias, 2001):

Conditions	Very mobile	Mobile	Somewhat mobile or scarcely mobile
Oxidising and acid, pH<3	Cd, Co, Cu, Ni, Zn	Hg, Mn, Re, V	All other PTEs
Oxidising in the absence of abundant Fe-rich particles, pH>5	Cd, Zn	Mo, Re, Se, Sr, Te, V	All other PTEs
Oxidising with abundant Fe-rich particulates, pH>5	/	Cd, Zn	All other PTEs
Reducing in the absence of hydrogen sulfide, pH>5	/	Cd, Cu, Fe, Mn, Pb, Sr, Zn	All other PTEs
Reducing with hydrogen sulfide, pH>5	/	Mn, Sr	All other PTEs

2.2.2 Bioavailability, translocation and uptake of the PTEs in the soil-plant system

Soil is defined as a product of the rock weathering formed by different physical, chemical and biochemical processes obtaining appropriate medium for growing plants. It is divided into layers so-called horisons. The horisons are forming by the weathering of parent rock, chemical processes, biological processes and the action of water including leaching from upper to lower horisons (Manahan, 2013). The following soil horisons are defined: O–organic soil layer, A–topsoil layer, B–subsoil layer and C–bedrock (FAO, 1998). In this doctoral dissertation, the depth of each investigated horison is defined between the soil layers (Figure 2.5). For plant growth, the most important is A-topsoil horison. Plant roots spread through the topsoil taking water and essential elements because this layer is mostly influenced by biological activities. The rhisosphere is the name for the part of topsoil with a high level of biomass that is composed of plant roots associated with the microorganisms. The root hairs surfaces are commonly colonised by microorganisms, which improve the uptake of essential elements by plant roots (Manahan, 2013).

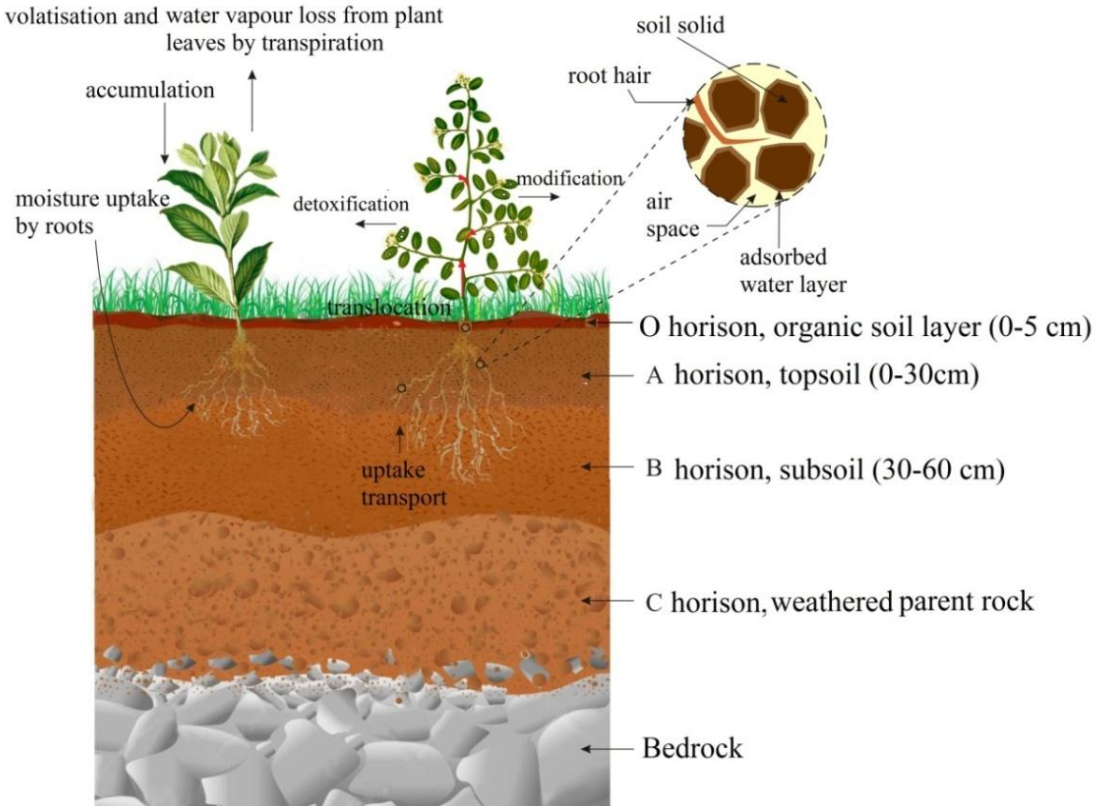


Figure 2.5 Soil structure showing a typical distribution of soil horisons resting on the parent rock; O–organic soil layer, A–topsoil layer, B–subsoil layer and C–bedrock; the figure shows aspects of soil microstructure including solid soil particles, water bound to soil particles, and its influence; the process of the elements uptake and translocation from soil to plant and further processes in plants (adopted and modify from Manahan, 2013).

All the properties, physico-chemical conditions and reactions in the soil influence the bioavailability of PTEs from soil to plant. In this doctoral dissertation, the term "bioavailability" will be used for assessing the elements availability from soil to different parts of the plant (grapevine). The bioavailability of PTEs is a variable process and is strongly controlled by specific properties of abiotic and biotic media as well as by the physico-chemical properties of the element. The mobility of PTEs in soil and its uptake by plants depend on various factors (PTEs concentration in soil, pH, soil organic matter (OM), CEC and Fe and Mn oxides content in soil) and the type of plant (Meeus et al., 2002; Khan et al., 2018). The root uptake of PTEs from soil and their translocation in plants and their parts is a very complex process. The root can absorb the PTEs both actively (metabolic) and passively (nonmetabolic). Newerhow, the contents of PTEs uptake are positively correlated with their available (mobile) element pool at the root surface. In the literature, the plant uptake of PTEs from soil has been assessed

by calculating the ratio of PTE concentration in the plant according to the PTE concentration in soil. In various studies, this factor has a different term e.g. Biological Absorption Coefficient−BAC, Index of Bioaccumulation−IBA or Transfer Factor−TF (Kabata-Pendias and Mukherjee, 2007).

It is widely known that plants are sorbing some quantities of nutrients and PTEs from the soil, and the element mobility and extractability from soils influence their bioavailability (Kabata-Pendias, 2004). The total element content in the soils represents a poor indicator of the elements bioavailability because the biodiversity is conditioned by different properties, conditions and reactions previously explained. Thus, beside the PTEs concentrations assessment, the measurements of physico-chemical parameters of the soil are important for the better understanding the potential bioavailability of various elements. Many single and sequential extraction procedures have been proposed to assess the mobility and bioavailability of metals in soils (Relić et al., 2005; Relić et al., 2010; Relić et al., 2013; Vázquez Vázquez, 2016).

The biochemical functions of many essential elements are already well known. Various PTEs are known to have a biological role, often as cofactors or part of the cofactor in enzymes and as structural elements in proteins, but these elements present or accumulated to the plant in exceeds can have toxic effects to plant or human. For other PTEs, known as non-essential the biochemical functions are not yet clearly understood (Kabata-Pendias and Mukherjee, 2007).

Plants uptake from the soil mostly those element quantities which are present in the soil solution (Figure 2.6). Thus, the binding of PTEs to soil constituents is one of the most important factors which are influencing their bioavailability. In addition, the roots have the ability to take up some quantities of PTEs present in soils in slightly mobile PTE forms because of different root exudates can change pH in the soil solution surrounding the root and then have an ability to chelate elements. In some highly polluted soils, the roots of plants may develop some specific mechanisms to protecting the plant from the high uptake of toxic elements (Manahan, 2013; Kabata-Pendias and Mukherjee, 2007 and references therein).

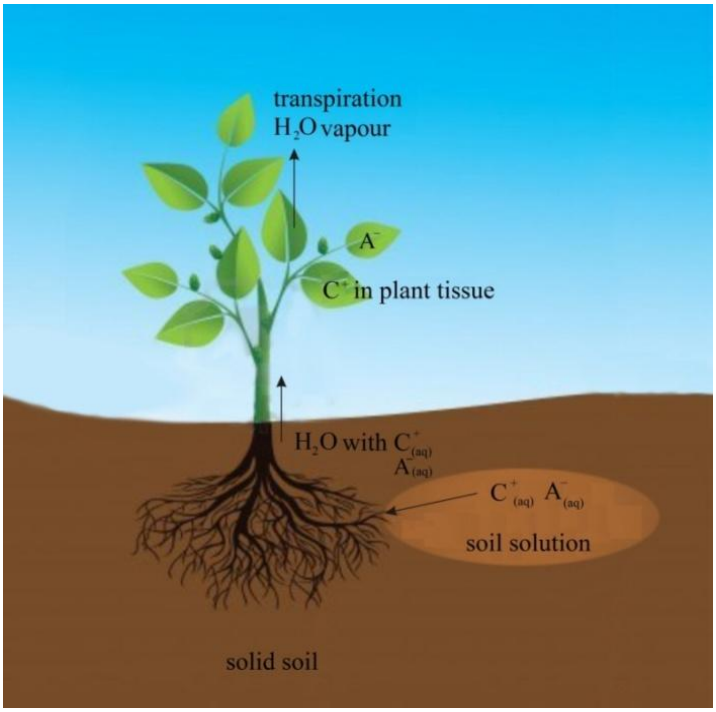


Figure 2.6 Soil cation exchange and uptake by plants: in the example shown, the element cation (C^+) is desorbed from soil into the soil solution, in which it is absorbed by a plant root and transported upward into the plant tissue by the osmotic flow of water and further translocated in different plant parts; the water eventually enters the atmosphere as water vapour through the process of transpiration, leaving the C^+ in the plant, where it participates in essential metabolic processes (adopted and modify from Manahan, 2013).

The investigation of element bioavailability from agricultural soil draws attention worldwide and has been ongoing for more than a few decades (Pelfrêne et al., 2012). In agricultural practices, various single extraction procedures have been used for estimating and assessing the bioavailable PTE pool. Therefore, it is important to highlight that the type of soils and plants species, climatic conditions and other environmental factors have a significant influence on the absorption of PTEs by roots, so any applied method must be related to specific conditions. For the evaluation of bioavailable PTEs based on single extraction procedures, various solutions have been used: mineral acids, chelating agents, buffered salts, neutral salt, and other solutions (for example in some studies *Coca-Cola*, which contains phosphoric acid, was used as the extractant). The most commonly neutral salt solutions (mainly $CaCl_2$, NH_4NO_3 and $NaNO_3$) and chelating agents (EDTA and DTPA) have been used (Quevauviller et al., 1996; Kabata-Pendias and Mukherjee, 2007; Ettler, 2016) as single extraction procedures. For example, the bioavailability of Cu, Zn, Ni, Cd and Pb has significantly

reduced if the soil pH is higher than 7 (Han, 2007). The absorption of various PTEs from soil to plant is mainly related to mass flow mechanisms and complex diffusion changes (Marschner, 2012; Bravo et al., 2017).

The general approach for assessing the PTE bioavailability has been to establish correlations or associations between PTEs in soil extracts (extracted by single extractions e.g. Na_2EDTA, $NaNO_3$, $CaCl_2$, NH_4NO_3, CH_3COOH, etc.) and the element concentrations measured in plants or plant parts. In addition, these single extraction procedures have also been used as secondary procedures for assessing bioavailability, without establishing correlations with the plant, and the PTEs concentration obtained in extracts have been named as bioavailable, plant-available, extractable or mobile fractions (Hooda, 2010). Overall, some of these single extraction procedures are widely accepted and applied in bioavailability assessment. Furthermore, it is important to standardise these single extraction procedures. Fortunately, there are some efforts performing due to standardisation issues. The Standards Measurements and Testing Programme of the EU (formerly Community Bureau of Reference, BCR) carried out several interlaboratory experiments and has provided indicative values for $CaCl_2$, $NaNO_3$ and NH_4NO_3 extractable PTEs in two sludge-amended soils and prepared a standard reference material (BCR CRM 483 and BCR CRM 484) (Queavauviller et al., 1997). Different single extractants e.g. $CaCl_2$, $BaCl_2$, $NaNO_3$ and NH_4NO_3 seem similar, but they have not been comprehensively compared thus far in any study worldwide, which has been done in this doctoral dissertation for the first time. Moreover, 0.1 M $NaNO_3$ (Bo, 1986) and 1.0 M NH_4NO_3 (DIN, 1995) have been adopted as national standard protocols in Switzerland and Germany, respectively (Pueyo et al., 2004), while 0.01 M $CaCl_2$ (Houba, 1996) has been recommended in the Netherlands (Pueyo et al., 2004) for similar metal testing protocols (Hooda, 2010). For example, $CaCl_2$ was also suggested by Houba et al. (2000) as the most suitable for a universal procedure for assessing risks from PTEs in soils, and also some other authors are recommending this protocol as suitable (Novozamsky et al., 1993; Houba et al., 2000; Peijnenburg et al., 2007). Even these protocols are becoming more useful because they are simple one-step extraction procedures, more effort should be applied for the comparative experiments due to their mutual comparison in order to find the most

efficient extractant for predicting bioavailability of soil elements that is one of the main aims established in this doctoral dissertation.

2.2.3 Air−soil and air−plant interactions

When the pollutants are once emitted to the atmosphere, the wind and atmospheric turbulences transport them. From the atmosphere, the pollutants are removing by the dry or wet deposition to surfaces (soil, plants etc.). Dry PM or PTEs deposition occurs through the gravitational settling and it is almost continuous. Bigger PM (diameter>10 μm) are quickly deposing while smaller PM can stay for days or months in the atmosphere (Grantz et al., 2003). Therefore, fine PM can pass large distance (1000–10000 km) before they deposed on the surface (WHO, 2005). Due to the short life (few minutes to hours), fine PM (e.g. $PM_{2.5}$ or $PM_{0.1}$) can grow rapid and associate in large aggregates by coagulation or condensation (Pope and Deckery, 2006) before deposing on the surface. Wet deposition is more effective for small PM and gases: raindrops growth in size and they could bound various pollutants during the deposition. Particles lower than 100 μm can be resuspended by wind, vehicle activities or tire wear (Nicholson, 1988). PM with diameter from 500 μm to1000 μm can move on the surface of the land (Kupiainen, 2007). The PM that is deposing on the surface can also influence the movement of another PM. Urban air quality is significantly attacked by the atmospheric PM and PTEs, but there are no many studies to confirm this for the rural areas.

Pollutants deposed on the soil surface sorb on the surface and further, they can be leached or due to another chemical process in soils can move through the soil layers depending on the soil and pollutant physico-chemical properties. Further, these pollutants can be accumulated to the plants by the root system. These chemical reactions of mobility and bioavailability of pollutants in the soil will be furthermore explained. Moreover, the pollutants entrapment on the plant surface and intercellular uptake of PTEs associated with PM (Brown and Bates, 1990) depend on ions which usually bound the differently charged sites at the cell wall and cause the ion exchangeability. Because PTEs originating from the air are not strongly bonded, they can be easily removed from the plant surface by washing or another process in the environment (rain or wind). In this reaction of ions exchange, the significant influence has H_2O (Bargagli,

1998), which can improve or reduce uptake of soluble ions which are bounded on the exchangeable form on the cell wall or plasma membrane surface of the plant. The insoluble PTEs may be stable, but rain can cause their mechanically remove. The plant can sorb PTE deposed on their surface by stomatal uptake, and further, the pollutant can be accumulated in the different plant tissue.

2.3 Environmental implications in the agricultural environment

Nowadays, various equations for assessing the environmental risk and environmental implications were developed. The soil contamination indices enable the normalisation of PTE concentrations to dimensionless-unit ”concentrations” which enable comparisons between the implications caused by PTEs (Kim et al., 2015; Antoniadis et al., 2017a, 2017b, 2017c), but the use of these indices is also appropriate for distinguishing pollution of different sites. By creating dimensionless-unit ”concentrations” soils may be more effectively classify according to contamination. Thus, these indices are important in monitoring areas polluted by PTEs. Also, normalisation of these values enables the mapping of soil pollution and enable the classification of pollution comparing the values calculated for different areas. All soil indices for assessment of the pollution are giving similar information: they obtained the ratio of PTEs in soil over the uncontaminated soil from the investigated area, usually termed as: ”background value” (Cao et al., 2010; Liu et al., 2005; Lin et al., 2016; Antoniadis et al., 2017a, 2017b, 2017c), ”background concentration” (Szolnoki and Farsang, 2013) or ”local background value” (the term which will be used in this doctoral dissertation). These “local background value” are characteristic only for the studied area because in sometimes researchers report these values as some values from the same potentially polluted soil or use those values from existing publications. It is important to note that background values could not be globally equal. They are rather site-specific for each investigated area. Three the most often applied indices of soil contamination are contamination factor (CF), geo-accumulation index (I_{geo}), and enrichment factor (EF). While CF and Igeo equations are based on the ratio of the element concentration in soil and concentration in the local background, in EF equation as “normaliser” commonly is used the most specific geogenic element (eg., Al, Fe or Mn), which probably is not contributing to the contamination of investigated soil. Index

values are classified for better evaluation and describing the pollution level of the site (Devesa-Rey et al., 2010; Sakan et al., 2014), assessing is PTE origin unknown or well-established (Lee et al., 1997; Ozkul, 2016). Indices have been used effectively in varied porous media apart from the soil, such as in river sediments (Duodu et al., 2016), as well as in different environmental matrices (Aiman et al., 2016). In addition, various other indices were developed such as potential ecological risk (RI) by Hakason (1980) and RI seems to be a suitable way to comprehensively express the PTE pollution (Hui-na et al., 2012; Ghasemi et al., 2018). Moreover, the bioavailability risks (BRAI) for the assessment of the risk caused by PTEs that are easily available was developed (Long et al., 1995; NOAA, 2004; Jamshidi-Zanjani et al. 2015). In addition, some equations were developed for better assessing the element bioaccumulation of PTEs from soil to plant (Biological accumulation concentration–BAC) (Radulescu et al., 2013; Bravo et al., 2017), which also can indicate if some plant species can be classified as metal excluder or hyper-accumulator. Finally, comparing the PTE concentrations between plant parts which are directly exposed to the atmospheric deposition with inner parts the (Ratio factor–RF) (Oliva and Mingorance, 2006) air pollution influence to the plant can be assessed.

In this doctoral dissertation, the environmental risk of soil and plant was assessed mainly comparing the PTE concentrations with local background values and various environmental implication equations were applied to estimate the level of pollution in the vineyard ambients.

2.4 Human health risk assessment in agricultural area

Human activities can increase the pollutant concentrations up to the phytotoxic level. In addition, for workers in the fields, who are chronically exposed to PTEs from the soil and directly exposed during agrochemical spraying treatments, these elements could cause serious health consequences (poisoning, respiratory diseases, even the carcinogenic diseases). PTEs in soils can affect human health through the inhalation of dust, ingestion of soil, or by dermal contact (Sylvain et al., 2016). The increased PTE concentration 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). In addition, PTEs can also contaminate plants growth on the soil

and subsequent with the products (fruits or vegetables) which are using as food can be intaken (Thron, 1996). The dietary intake of PTEs present in fruits or vegetables, especially products growth on potentially polluted agricultural areas (parcels near industries, foundries or highway roads) is very important (Guerreiro et al., 2016; Thron, 1996).

There are different models that can be found and used for human health risk assessment applying the concentrations of measured pollutants in soil or fruit 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 Environmental Protection Agency of United States (US EPA) guidance for human health risk assessments and adequate equations are published at *The Risk Assessment Information System, RAIS* (RAIS, 2013). Besides this model, there exist some other models such as contaminated land exposure assessment (CLEA) and an exposure model for human risk assessment of soil contamination (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 the UK and Dutch Environmental National Agencies.

The equations available at *The Risk Assessment Information System, RAIS*, adapted to the local conditions, were used in this doctoral dissertation (RAIS, 2013) for the health risk assessment for the field workers and grape and wine consumers.

2.5 Biomonitoring of air quality

Biomonitoring represents the different organisms' (plants or animals) response to the pollutant presence in the environment (Bargagli, 1998; Wolterbeek et al., 2002; Markert, 2007). Thus, organisms, part of organisms or communities of organisms that contain information on the quality of the environment represent **bioindicators** and which can give relevant information about the quality of the environment. In addition, organisms, part of organisms or communities of organisms containing information on a quantitative aspect of the quality of the environment or part of the environment represent **biomonitors**. The well-chosen biomonitor is a species that can reflect the quantitative composition of the ambient. However, due to the complexity of environmental abiotic and biotic factors, bioindicators/biomonitors have the capability

to take up the pollutants through two mechanisms biomagnification (sorption of substances from nutrients through the digestive tract or respiratory system−characteristic for animals) and bioconcentration (direct sorption of substances from the environment through the tissue-specific for plant biomonitors).

Among the different species, a reliable bioindicator should be chosen according to the following characteristics: ability to accumulate high levels of pollutants, sensitivity to specific air pollutants, availability to represent local pollution, abundance and wide distribution of the bioindicator, life-long enough due to temporal comparisons, easy for sampling, ability to accumulate the concentration quantities which are measurable by referent analytical techniques (Zhou et al., 2008).

Commonly regarded the best air pollution indicators are mosses and lichens due to their ability to accumulate PTEs in high levels (Rühling and Tyler, 1968; Berg and Steinnes, 1997; Harmens et al., 2008; Aničić et al., 2009a, 2009b, 2009c). However, in "anthropogenically devastated areas" (such as industrial areas, urban or agricultural areas), apart from mosses and lichens, other plants can give a reliable information about the ambient pollution. The main advantages of using leaves for air monitoring are their greater availability and large surface, the simplicity of species identification, sampling and treatment, and their possibility to cover large areas. Hence, the leaves have been used as ambient pollution indicators in polluted areas where lichens and mosses are often absent (Bargagli, 1998; Hoodaji et al., 2012). In addition, the accumulation of PTEs by plants primary depends on the root system, binding and solubility of deposed particles on the leaves. To monitor or assess the level of pollution in potentially polluted areas, different leaf species are studied as bioindicators (Turan et al., 2011). Among the leaf species, the ability to indicate the ambient pollution greatly varies (Bargagli, 1998; Weiss et al., 2003; Tomašević et al., 2004; Tomašević et al., 2005). The grapevine leaves have been analysed in various studies in order to improve the plant nutrition or to test PTEs influence on grapevine but according to best of my knowledge, there is not yet published any study where the grapevine (*Vitis vinifera L.*) leaves were tested as potential air pollution biomonitors.

As previously mentioned, mosses represent one of the best bioindicators for air pollution assessment. They represent primitive organisms without vascular tissues characteristic for vascular plants (e.g. root, stem and leaf). They occur on a wide range

of substrates e.g. soil, rock, bark, wood and even leaf cuticles (Vanderpoorten and Goffinet, 2009). The mosses are held on the substrate by rhizoids. Thus, the above-ground moss part (cauloid) collects nutrients, H_2O and PTEs directly from precipitation and dry deposition from the atmosphere and only non-significant quantities of the elements could originate from the substrate (Market et al., 2003). In addition, mosses have some other morpho-physiological characteristics, such as a large surface and undeveloped cuticle on the surface and high ability to exchange the cations through the surface entrapment or intercellular uptake (Brown and Bates, 1990; González and Pokrovsky, 2014). They also have the capacity to tolerate dehydration and to recover from it without physiological damage. Due to their morpho-physiological characteristics and cosmopolitan abundance, mosses have high advantages as bioindicators of air pollution by organic and inorganic substances (Bargagli, 1998, Markert et al., 2003).

In almost last six decades, mosses as air quality bioindicators have been studied by worldwide (Rühling and Tyler, 1973). Many studies were performed in order to investigate different mosses as biomonitors of inorganic and organic pollutants (Aničić Urošević et al. 2017, and references therein).

Finally, the methods with instrumental sampling are usually limited by the high-costs and it is not easy to perform spatio-temporal monitoring. Thus, moss bag biomonitoring offers cost-effective and easy performable technique giving information about ambient quality (Markert, 1995; Bargagli, 1998; Weiss, 2003; Rucandio et al., 2011).

Generally, two different approaches in biomonitoring of pollutants are defined as passive biomonitoring, using the organisms naturally occurring in the environment and active biomonitoring using biomonitors prepared in the laboratory conditions or growing at the pristine area and exposed in a standardised form in the polluted area where naturally growing biomonitor is absent (Markert, 2007).

2.5.1 Active moss bag biomonitoring

Active moss bag biomonitoring give great possibilities of technique application in various ambient for assessing the air quality due to the possibility to control many measurement parameters (the exposure time, measuring site/position and initial concentration). Although, the mosses are widely distributed, there are some areas where

mosses are not present, such as urban, industrial or agricultural. In urban areas, dominant landscaping makes the cities into "moss deserts". The agricultural areas with extensive plant cultivation are also recognised as ambient with moss absence. To overcome the moss absence from some ambient, the active biomonitoring approach enables to assess air pollution by moss biomonitors. This approach represents transplantation of mosses from unpolluted pristine area to the polluted areas. According to the literature, the most common active biomonitoring using mosses is moss bag technique, which has been introduced by Goodman and Roberts (1971). Furthermore, the technique was modified regarding the moss species choose, different pre-treatments, preparation of bags for exposure and the exposure time (Ares et al., 2012). However, for this technique, there are still not adopted unique international standards, but for example in Finland, this technique is nationally standardised (SFS 5794 Finnish Standards Association 1994). The comprehensive review of the moss bag technique application over urban and industrial areas is given by Ares et al. (2012) and Aničić et al. (2017).

Because it is characterised by a lower variability of the measured concentrations between the subsamples, lower initial pollutant level, controlled time of mosses exposure, minimises the abiotic factors that could influence the element concentration, overcomes the inaccessibility of many sampling sites, the active moss bag biomonitoring has some advantages in comparison to the passive approach. The disadvantage of the technique represents losing the moss vitality due to it transplantation from the natural habitat. Moreover, during the exposure, the moss tissue growth can "dilute" the real concentrations of pollutant, so before the transplantation the mosses in the bags the moss devitalisation is recommended due to avoiding the moss growth, especially if they are exposed in humid climate zone (Fernández et al. 2010).

Active moss biomonitoring has been applied mostly in urban and industrial areas and very rare in agricultural areas (Ares et al. 2012; Capozzi et al. 2016a). In the last 13 years, the crucial variables improving the methodological approach of the moss bag technique application (species-specific and the time- and site-dependent pollutant enrichment) through a various studies were performed in urban area of Belgrade (Aničić et al. 2009a, 2009b, 2009c; Vuković et al. 2013, 2014, 2015a; 2015b, 2016, 2017). Thus, in this doctoral dissertation for the first time the moss bag biomonitoring will be

performed in the agricultural area in Serbia and specifically, in the vineyard ambient, the moss bag technique has not been applied worldwide yet.

The exposure period of ten weeks is proposed to obtained satisfactory PTE enrichment in moss bags. According to a review publication (Ares et al., 2012), ten weeks of exposure was proposed for further studies. However, the PTE concentrations in the moss bags have a tendency to increase with the exposure time prolongation (from 1 to 5 months) (Aničić et al., 2009c). Moreover, during the first ten weeks, the most PTE concentrations in the mosses increase, even for the REEs the same trend was observed.

2.5.2 (Bio)monitoring of magnetic particles

Application of magnetic measurements in environmental studies is based on the fundamental nature of magnetism and the presence of Fe. Thus, the methods based on magnetic measurements are built on the mineral-magnetic principles of rock- and palaeomagnetism (Dekkers, 1997; Salo, 2017) and can indicate Fe-bearing minerals and magnetic PM grain sizes, concentration and composition. With these minerals and magnetic PM are usually associated with PTEs. Thus, for monitoring of magnetic PM, the magnetic parameters can represent an alternative and complementary method for environmental pollution assessment. Instrumental PM monitoring with high spatio-temporal resolution requires expensive equipment and continuous maintenance of the monitoring stations. Application of magnetic methods for assessing the magnetic PM has some advantages such as the necessity of fast measurements and a small sample quantity for analysis. Also, these methods for obtaining magnetic parameters such as of magnetic susceptibility and saturation isothermal remanent magnetisation are cost-effective, sensitive and non-destructive (Wang et al., 2018). Overall, magnetic methods represent a proxy for quickly screening of the PM pollution over large areas (Salo, 2010). Combination of magnetic and geochemical methods has been applied in many studies for assessing air, soil or sediment pollution and also this method was used for quantification of magnetic PM originating from anthropogenic sources (Wang et al., 2018).

The magnetic parameters determination have been useful for preparing maps of the topsoil magnetic properties for national soil investigations in Austria (Hanesch et al.,

2007), Bosnia and Hercegovina (Hannam and Dearing, 2008), England and Wales (Blundell et al., 2009), France (Thiesson et al., 2012), Poland (Łukasik et al., 2016) and Bulgaria (Jordanova et al., 2016; Wang et al, 2018). Nowadays, the magnetic parameters are applicable for the semi-quantification some of the PTEs (e.g. Cu, Pb, Zn, Cr, V and Mn) (Hu et al., 2008; Zhang et al., 2011; Karimi et al., 2011; Qiao et al., 2013; Wang et al., 2013; Wang et al., 2018).

Previously described biomonitoring based on PTEs determination in plant leaves imply them as a potentially good indicator for urban ambient quality (Tomašević et al., 2004; Balasooriya et al, 2009; Kardel et al., 2010, 2011). Moreover, leaf magnetic parameters such as magnetic susceptibility and saturation isothermal remanence magnetisation have been reported as a valuable proxy for magnetic PM pollution on leaf surfaces (Mitchell et al., 2010; Hansard et al., 2011; Kardel et al., 2012). Leaf biomonitoring of magnetic PM is a cost-effective technique which allows obtaining large spatio-temporal information of pollution. It is possible to combine different species for obtaining pollution covering the investigated area (Kardel et al., 2012). The disadvantage of the magnetic PM biomonitoring using leaves can be the absence of plants, but this can be overcome by an active biomonitoring (Vuković et al., 2015a, 2015b).

Studies of biomonitoring of magnetic PM on vegetation samples (tree leaves, needles, tree ring cores, mosses, lichen) have been carried out almost last two decades (Flanders, 1994; Matzka and Maher, 1999; Moreno et al., 2003; Hanesch et al., 2003; Gautam et al., 2005; Lehndorff et al., 2006; Maher et al., 2008; Zhang et al., 2012; Castañeda Miranda, 2014; Castañeda Miranda, 2016; Jordanova et al., 2016; Hofman et al., 2017 and references therein; Rachwał et al., 2018). The results from various studies imply that some PTEs (e.g. Cu, Cr, As, Zn and Pb) formed during fossil fuel combustion processes could be associated with magnetic Fe-oxides (Boyko et al., 2004; Desenfant et al., 2004; Magiera et al., 2013; Wang, 2018). All these publications demonstrated the leaf potential as passive magnetic PM collectors which can indicate environmental pollution. However, in this doctoral dissertation for the first time, the grapevine leaves have been used in comparison to the PTE concentrations for the assessment magnetic parameters as a proxy for ambient environmental pollution in the vineyard.

3 Materials and methods

3.1 Study areas

From 2014 to 2018, six experiments were conducted in three different grapevine growing areas (experimental, commercial and organic vineyards) located on the territory of the Republic of Serbia (Figure 3.1).

The experimental vineyard "Radmilovac" is located in a suburban settlement of Belgrade, (44°45'24"N; 20°34'54"E) (Figure 3.1), the capital of Serbia, in "Belgrade" grapevine growing subregion (Ivanišević et al., 2015), in "Gročansko" vineyard area. This vineyard is a conventionally grown, but because of the frequent experimental activities in the agriculture field and new varieties production, further, it will be named *experimental vineyard.* The experimental vineyard "Radmilovac" covers an area of 88 ha. The vineyard parcels are located between the Institute of Nuclear Research "Vinča", the hazardous waste landfills and the highway road. The institute landfill is oriented towards the vineyard parcels of vineyard area "Radmilovac". This area is hilly and due to the position between the Danube River and Pannonia basin from one side and Avala mountain and Belgrade city from the other, this area is characterised by the eastern-continental climate. The vineyards in this region extend at the altitude from 150 to 250 m. The slope of the terrain is moderately steep to mild (Ivanišević et al., 2015). All the parcels (T1−T6) are grouped as a complement field, except T10, P and C. Parcel C represents a control sampling site located in the surround of the investigated vineyard and represents a local background sample. Parcel T6 is located near the main road and parcel T5 is located 1.5 km from the Institute of Nuclear Science "Vinča" (Figure 3.2). Experiment 1 from this dissertation was conducted in this vineyard during the harvest (August).

The agricultural subregion "Oplenac Wine Route" (44°13′36.3″N; 20°39′12.4″E) is well-known grapevine growing area in Serbia (Figure 3.1) located in "Šumadija" grapevine growing subregion (Ivanišević et al., 2015). The sampling sites were located in the village, near the Topola town, 80 km from Belgrade. This vineyard is conventionally cultivated for the commercial vine production and further, it will be named *commercial vineyard.* In this area, six vineyard parcels (I, II, III, IV, V and VI) were investigated. The potential pollution sources, metal foundry near the parcel VI and the highway road near the parcels I, IV and V, were positioned close to the investigated

vineyard area. The highest distance between the parcels was 2 km (between the parcels IV and V). The parcels I, II, III were located next each to other and they were separated from the parcel IV by the road. The parcel V is located 800 m from the parcel VI which is the only investigated parcel that is sheltered from the road influence by the building of the metal foundry. The studied soils were alluvial colluvial (Coluvic Regosol), very carbonated, sandy clay and poorly enriched by the hummus (Ninkov et al., 2014). The studied parcels were in the system of no-tilling grapevine production and they were not located on the slope terrain. In the studied region, precipitations were the most frequent from March to June (before the harvest) in 2015 (Republic Hydrometeorological Service of Serbia), (Figure 3.3). The experiments 2, 3, 4 and 6 were conducted in this commercial vineyard through the entire grapevine season (from pre-agrochemical treatment period−April to harvest period−August).

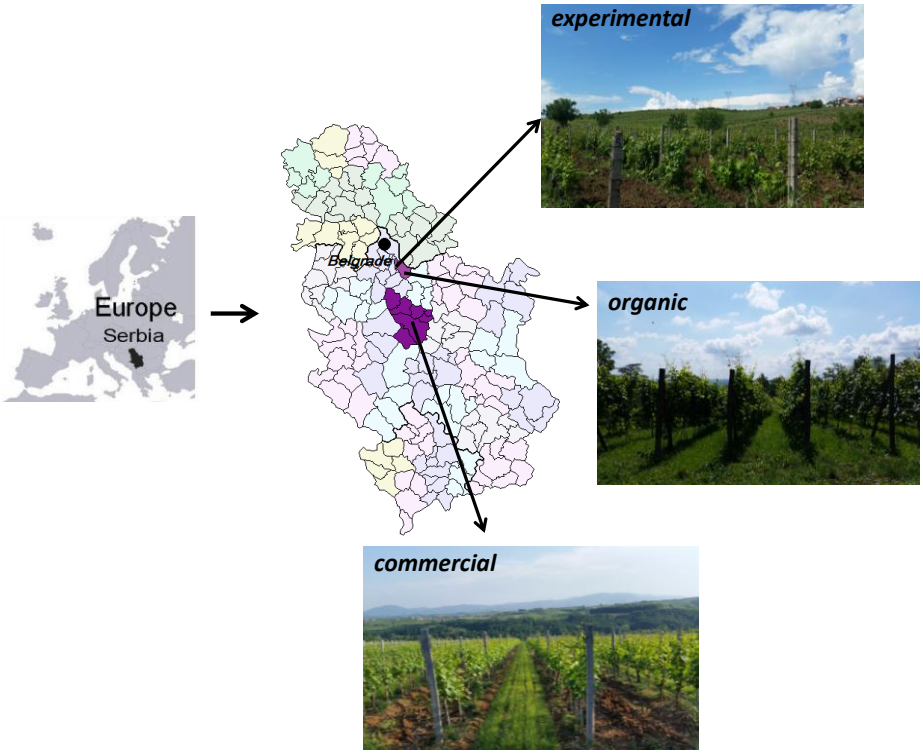


Figure 3.1 The locations of the investigated vineyard areas in Serbia.

The third investigated vineyard is one of three organic growth vineyards in Serbia. It is located in ”Grocka” near the Danube river (Figure 3.1). “Grocka” is a suburban municipality of Belgrade (Figure 3.4). It is located in Belgrade grapevine

growing subregion, in "Gročansko" vineyard area (Ivanišević et al., 2015). In the past, this area was well known as "Indigo hills" because the vineyards had grown in this region was frequently treated by the copper (II) sulphate and these fields looked like indigo blue hills. During the XX century, the different fruits were produced in this area. From 2008 the *organic vineyard* was grown in this place. The vineyard is located on a terrain slope of 10%, orientated south-east, at the altitude from 145 m to 195 m, or about 80 m above the Danube River level. The parcel 1 is located from the Danube River around 1 km. Parcels 2 and 3 are located 3 km from parcel 1. The parcels 4 and 5 are located 300 m from the parcel 1 (Figure 3.2), near the Danube River. In this vineyard, two experiments were conducted (5 and 6) in the most specific periods for the grapevine growth (leaf set–June, veraison–July and harvest–September).

3.2 Sampling

3.2.1 Soil samples

In the studied vineyards, sampling was performed from 2014 to 2016 during the grapevine seasons. Three soil layers were sampled: organic soil layer (0–5 cm), topsoil (0–30 cm) and subsoil (30–60 cm). The soil samples were collected using the sampling probe (Figure 3.5a), 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 marked plastic bags (Figure 3.5b) and transported to the laboratory. The control samples (marked in different experiments as C−Experiments 1, 2, 3 and 6) for the determination of the local background values of the measured elements in the soil were sampled from the same area, in the surrounds of the grapevine growing parcels, but the location was not exposed to any agricultural activities or plant growth. In the case of Experiment 5, conducted in the organic vineyard (where the agrochemicals were not or in low quantities were used), local background samples represent the deepest sampled soil layers in each of the investigated parcels (30−60 cm).

In the *experimental vineyard*, the topsoil samples (0–30 cm) were collected from nine different vineyard parcels, marked as tables T1, T2, T3, T4, T5, T6, T10, P and C during the harvest 2014. In each parcel, the soil samples were taken as the composite samples of 10 subsamples sampled along the diagonal of the parcel. The samples T2 and

T4 were collected from the central part of the vineyard area. The P table is located close to the local stream and tables T1, T5 and K are experimental fields without grapevine. Table C was used as a control sample for the determination of the local background values of the measured elements (Figure 3.2).

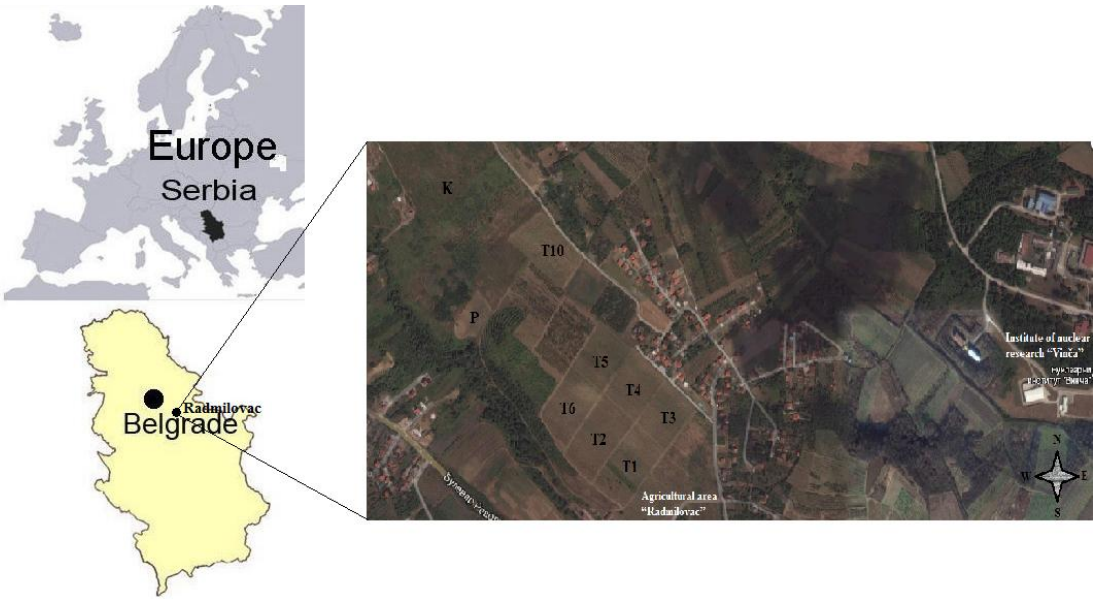


Figure 3.2 Location of the investigated experimental vineyard parcels (Milićević et al., 2017a).

In the *commercial vineyard*, the soil samples were collected from the six vineyard parcels (I, II, III, IV, V and VI) (Figure 3.3) from two different depths (0−30 cm and 0–60 cm) through the entire grapevine season (from April to October) 2015. The soil was sampled along transects in each of the investigated vineyard parcels, moving from the potential pollution sources (highway road or metal foundry; Figure 3.3).

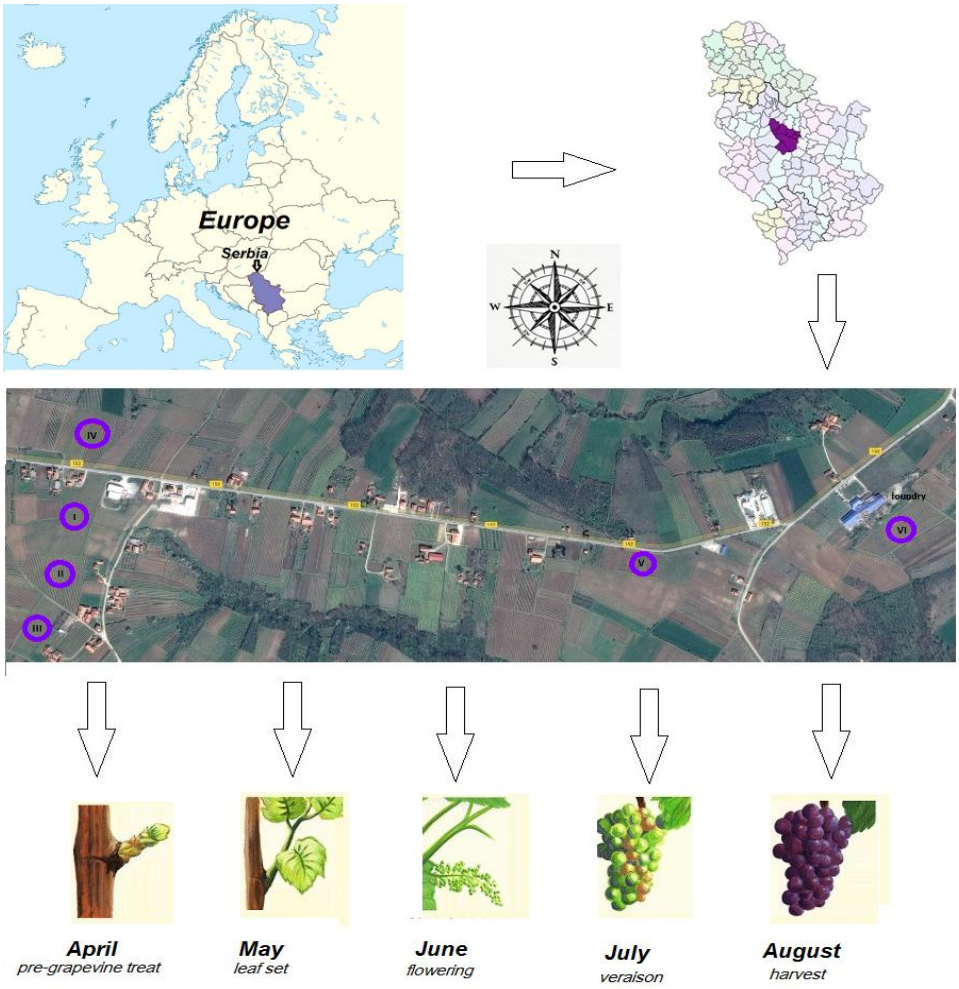


Figure 3.3 The location of the investigated experimental vineyard and position of the investigated parcels and illustration of grapevine growing phases; Experiment 2 was conducted during the harvest period (soil, grapevine parts−seed, pulp, skin, whole berry, leaf and wine were sampled) among investigated parcels; Experiment 3 was conducted (soil and leaves were collected) among all parcels through the entire grapevine season; Experiment 4 was conducted exposing moss bags among investigated parcels during the entire grapevine season; The metal foundry near the parcel VI and highway road near the parcels I, IV and V are located (Milićević et al., 2018b).

In the *organic vineyard*, the soil samples from three different depths (0−5 cm; 0−30 cm and 30−60 cm) were collected from five different parcels during 2016. From each parcel, the composite sample prepared of 10 subsamples were collected along transects in the investigated parcels (Figure 3.4), as in experiment conducted in the *experimental vineyard*. The local background samples represent the subsoil samples (30–60 cm) in the organic vineyard parcels (Figure 3.4). Because in the organic vineyard there were not frequent agricultural activities the sampling was performed starting from June to September to cover all important grapevine growing phases (leaf set, veraison and harvest).

Figure 3.4 The location of the investigated organic vineyard and the position of the parcels; The parcels 4 and 5 are located near the Danube River.

3.2.2 Grapevine samples

In three investigated vineyards, 11 grapevine (*Vitis vinifera* L.) varieties were sampled (*Cabernet sauvignon, Riesling italian, Riesling rain, Burgundac, Prokupac, Cabernet franc, Merlot, Sauvignon blanc, Regent, Panonia*) during the grapevine harvest. From each of the varieties, the grapevine leaves and grapevine berries were sampled at the same sampling sites where the soil was sampled (Figure 3.5,d).

In the *experimental vineyard*, seven different grapevine (*Vitis vinifera* L.) varieties were sampled. They were grown by the following order: T2–*Riesling rain* and *Burgundac*, T3–*Cabernet sauvignon* and *Riesling italian*, T4–*Prokupac* and *Cabernet sauvignon*, T6–*Cabernet franc*, T10–*Cabernet franc* and *Merlot*, P–*Cabernet franc*. For the need of the pilot study, the grape leaf and grape berries were sampled from each of the parcel (tables: T2, T3, T4, T6, T10 and P) (Figure 3.2).

In the *commercial vineyard*, *Sauvignon blanc* from parcels I, II, III, IV and VI; and *Cabernet sauvignon* from parcel V were sampled. Leaf samples were collected from each of the sampling sites through the entire grapevine season (from leaf set

phase−May to harvest phase−August). Grapevine berry samples were collected during the grapevine harvest 2015. The wine samples (red and white wine) were prepared from the grapes collected during the studied harvest from the investigated parcels (Figure 3.3).

Two grapevine (*Vitis vinifera* L.) varieties were sampled in the organic vineyard, *Pannonia* and *Regent*. Leaf and petiole samples were collected through the season (June−leaf set, July−vearison and September−harvest) and grapevine berries in the harvest 2016.

Figure 3.5 a) Soil sampling by the probe; b) soil samples packing in the plastic bags; c) leaf sampling; and d) grape sampling performed in the investigated vineyards.

3.2.3 Moss sampling and moss transplantation

Two moss species (*Sphagnum girgensohnii* Russow−*S. girgensohnii* and *Hypnum cupressiforme* Hedw.−*H. cupressiforme*) were chosen for the moss bag biomonitoring of the air pollution in the *commercial vineyard* (Experiment 4) and *S. girgensohnii*, that is the most sensitive moss genera and the most recommended, was used for the biomonitoring in the *organic vineyard* (Experiment 5). The moss *S. girgensohnii*[1] was collected at the end of May 2014 from a pristine wetland area located

[1] permit for import this moss type from the area where it is widely present and not under protection as an endemic species (country of origin: Russia, 'Domkino' site) was obtained from the competent ministries;

in the vicinity of "Domkino", Dubna, Russia (Figure 3.6 a). Based on the previously published studies (Aničić et al., 2009a; Vuković et al., 2016), this location is well-known as an appropriate background area.

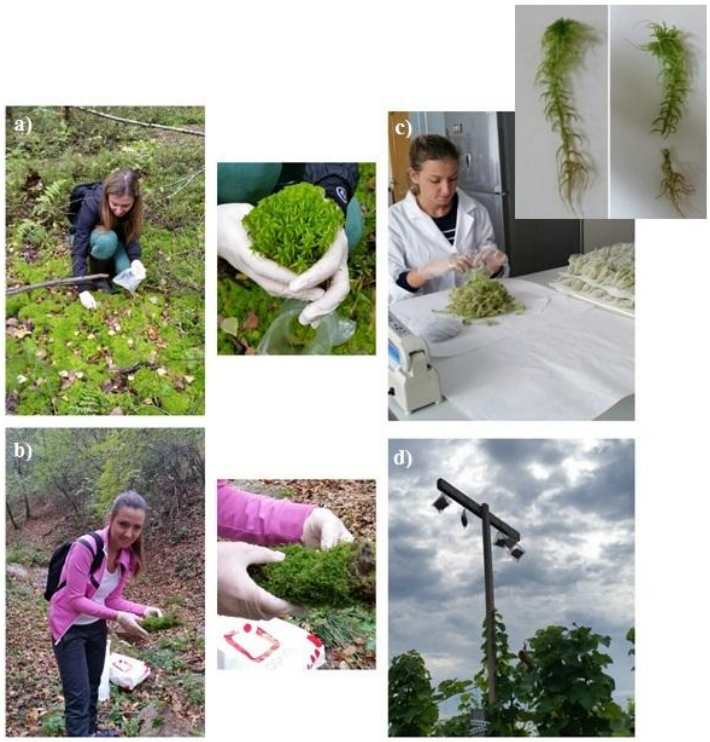


Figure 3.6 a) Moss *S.girgensohnii* sampling; b) moss *H.cupressiforme* sampling c) moss cleaning and transplantation in the bags; and d) moss bags exposure in the vineyards.

Another one moss specie is naturally and widely present in the territory of Serbia. The moss *H. cupressiforme*[2] was collected from the location "Vršačke planine", which is defined as the protected area in Serbia (Figure 3.6b). The moss material preparation and the moss bags exposure were performed according to the recommendations given in the review of Ares et al. (2012). The moss bag shape and duration of bags exposure were chosen in order to be comparable with the previous research conducted in Serbia (Aničić et al., 2009a, 2009c; Vuković et al., 2015a, 2015b, 2016). In the laboratory, the green apical parts of the collected mosses were separated from the rest of brownish tissue and manually cleaned from extraneous material, i.e., soil particles, leaves, pine needles (Figure 3.6c). Further, the moss was washed thrice

the total quantity of the imported moss is ≈1 kg of semi-weighted mass, packed in bags (≈1 g) used for the exposure on the sites for the purposes of scientific research (non-commercial use); Imported species of moss does not endanger the biodiversity of indigenous species.

[2] this moss species is widely present in Serbia and is not protected as an endemic species

with double distilled water (100 g of the fresh moss weight was shaken with ≈10 L of the double distilled water). Prepared like this, the moss was air dried and gently hand-mixed to obtain a homogeneous material. Approximately 1.5 g of the homogeneous moss material was packed in flat 7×7 cm nylon net bags with a mesh diameter of 2 mm. In order to eliminate possible contamination, prior to use, the mesh was washed using 0.1 mol L^{-1} HNO_3. The moss bag dimension and the moss weight inside were selected to achieve a mass-to-surface ratio of approximately 30 mg cm^{-2} (Figure 3.6c). Finally, prepared moss bags were exposed in the *commercial* and the *organic* vineyards for assessing the air quality in agricultural ambient (Figure 3.6d).

3.3 Samples preparation for the analyses

3.3.1 Soil samples preparation for the destructive and non-destructive analyses

Each soil sample analysed in all experiments was air-dried in the laboratory. During the drying the soil samples were covered with the filter paper. After the drying, the samples were sieved through a 2 mm stainless sieve (Figure 3.7a) and ground to a fine powder in an agate mortar with a pestle (Figure 3.7b).

Figure 3.7 Soil sample preparation for the analyses: a) sieving through a 2 mm stainless sieve; b) grounding to a fine powder in an agate mortar with a pestle; c) the leaf drying d) the leaf grounding; and e) the grapevine samples preparation (separating the skin, pulp, seed and whole berries) for the elements' determination.

Before the chemical analyses, the physico-chemical parameters of the soil samples were determined. The hygroscopic moisture of each soil sample was determined at 105°C until the dry weight (Figure 8.1.1d, Appendix 1). All the chemicals used in the experiment were of analytical grade (puriss p.a.) and produced by Sigma-Aldrich. For obtaining the best analysis, removing all contaminants, the acids were distilled (Figure 8.1.1a, Appendix 1). In addition, the deionised water was cleaned to ultra-pure water (Figure 8.1.1b, Appendix 1). All the laboratory glassware for the samples preparation for PTE concentrations determination was washed in the following order: H_2O and detergent, 10% HNO_3 and deionised H_2O. The acidity (pH) of the soil samples was determined in a mixture (1:5) of soil–distilled H_2O, soil–1 mol L^{-1} KCl and soil–0.1 mol L^{-1} $CaCl_2$ using Professional Multi-Parameter pH/ORP/Conductivity/TDS/TEMPERATURE Bench Meter with GLP−AD800 (Figure 8.1.1c, Appendix 1). The soil organic matter (OM) was determined by weighting the soil samples at 105°C and 360°C using the procedure adopted by Storer (1984). Different extraction solutions were used for assessing element mobility and bioavailability from the vineyard soil: 0.11 mol L^{-1} CH_3COOH during 16 h, 0.44 mol L^{-1} CH_3COOH during 16 h, 0.05 mol L^{-1} Na_2EDTA during 1 h, 0.01 mol L^{-1} $CaCl_2$ during 3 h, 1 mol L^{-1} $BaCl_2$ during 3 h, 0.1 mol L^{-1} NH_4NO_3 during 2 h, 0.1 mol L^{-1} $NaNO_3$ during 2 h and deionised H_2O during 2 h and 16 h (Ure, 1996; Quevauviller, 1998; Quevauviller, 2002; Pueyo et al., 2004; Table 3.1). The single extraction procedures were performed on an over-head rotary shaker (Figure 3.8a,b) in a specific way that is more detailed explained in Table 3.1. The samples were centrifuged after the extraction at 3000 rpm for 10 min (Figure 8.1.1e, Appendix 1). The supernatants were separated from the precipitate through the filter paper (Filter paper, Blue Ribbon, Grade 15 (2–3 pm), Ø125 mm, producer FIORONI) (Figure 3.8c). The pseudo-total digestion was performed using an aqua regia solution in a microwave oven (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy) in sealed PTFE vessels using 9 mL of HCl and 3 mL of HNO_3 for 0.5 g per each soil sample (US EPA 3050b, Method, Table 3.1) (Figure 3.8d). After the extractions and digestion, the samples were filtered through the filter paper (Filter paper, Blue Ribbon, Grade 15 (2–3 pm), Ø125 mm, producer

FIORONI) and packed in the polyethylene bottles until the element determination (Figure 3.8e,f).

Figure 3.8 a) Soil extraction on the rotary shaker; b) centrifuged (left three cuvettes) versus non-centrifuged (right three cuvettes) soil extracts; c) the supernatants separating from the precipitate through the filter paper after the extraction; d) soil and plant material microwave digestion; e) filtering and packing in polyethylene bottles after the soil and the plant material microwave digestion.

Table 3.1 Procedures for PTE single extractions and pseudo-total digestion of the soil samples and digestion of the plant material (leaf, petiole, berry, skin, pulp, seed and transplanted mosses)

Extractant	Type	Procedure	References	Experiment
		soil samples		
Deionised water	water-soluble soil pore water	2 g of each soil sample was measured and 20 mL of distilled water was added. The extraction was performed for 16 h on a rotary shaker.		1, 2, 3, 5
Deionised water	water-soluble soil pore water	2 g of each soil sample was measured and 20 mL of distilled water was added. The extraction was performed for 2 h on a rotary shaker.	Pueyo et al., 2004;	1, 2, 3, 5
0.01 mol L^{-1} $CaCl_2$	exchangeable	2 g of each soil sample was measured and 20 mL of extractant was added. The extraction was performed for 3 h on a rotary shaker.	Pueyo et al., 2004; Quevauviller, 1998.	1, 2, 3, 5
1 mol L^{-1} $BaCl_2$	exchangeable	2 g of each soil sample was measured and 20 mL of extractant was added. The extraction was performed for 3 h on a rotary shaker.	Sumner and Miller, 1996	5
0.1 mol L^{-1} NH_4NO_3	exchangeable	4 g of each soil sample was measured and 10 mL of extractant was added. The extraction was performed for 2 h on a rotary shaker.	Quevauviller, 1998.	1, 2, 3, 5
0.1 mol L^{-1} $NaNO_3$	exchangeable	4 g of each soil sample was measured and 10 mL of extractant was added. The extraction was performed for 2 h on a rotary shaker.	Quevauviller, 1998.	5
0.05 mol L^{-1} Na_2EDTA	organically bound	2 g of each soil sample was measured and 20 mL of extractant was added. The extraction was performed for 1 h on a rotary shaker.	Pueyo et al., 2004; Quevauviller, 1998.	1, 2, 3, 5
0.11 mol L^{-1} CH_3COOH	carbonate	1 g of each soil sample was measured and 40 mL of extractant was added. The extraction was performed for 16 h on a rotary shaker.	Quevauviller, 1998.	1, 2, 3, 5
0.44 mol L^{-1} CH_3COOH	carbonate	1 g of each soil sample was measured and 40 mL of extractant was added. The extraction was performed for 16 h on a rotary shaker	Quevauviller, 1998.	5
Aqua regia (HNO_3 : HCl)	pseudo-total	0.5 g of each soil sample was digested using 9 mL 35% HCl and 3 mL 65% HNO_3	US EPA 3050b Method	1, 2, 3, 5
		grapevine samples (leaf, petiole, berry, skin, pulp, seed) and transplanted moss samples		
HNO_3 : H_2O_2	total	0.5 g of each leaf, petiole and seed samples were digested using 1 mL 30% H_2O_2 and 7 mL of 65% HNO_3	US EPA 3050 Method	1, 2, 3, 5
HNO_3 : H_2O_2	total	1 g of each berry, skin and pulp samples were digested using 1 mL 30% H_2O_2 and 7 mL of 65% HNO_3	US EPA 3050 Method	1, 3, 5
HNO_3 : H_2O_2	total	0.3 g of each moss sample was digested using 1 mL 30% H_2O_2 and 7 mL of 65% HNO_3	US EPA 3050 Method	4, 5

For the non-destructive soil sample analyses, the samples were dry until the dry mass. For samples preparation for the element analysis on WD-XRF, the dry mass (5 g ± 1 mg) of each soil sample was mixed with the wax (20% from the dry soil mass). The pellets were prepared in the press, 2 min on 5 bars and then 5 minutes on 15 bars. The element concentrations in the pellets were measured by wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) (Figure 3.9). For the determination of the total content of C, N, H and S in the soil, approximately 1 g of the dry and grounded soil samples were analysed.

Figure 3.9 Soil and leaf preparation of the pellets for the element analysis by WD-XRF.

For measuring magnetic parameters, the soil samples, approximately 0.5 g of each, were carefully packed in the clean foil and then in the polyethylene containers (volume 10 cm^3) (Figure 3.10a,b).

Figure 3.10 a) Soil samples preparation for the SIRM and Susceptibility analyses and b) leaf.

3.3.2 Grapevine and moss samples preparation for the destructive and leaf sample preparation for the non-destructive analyses

All the chemicals used in the experiment were of analytical grade (puriss p.a.) and produced by Sigma-Aldrich. Aiming to remove all impurities, the acids were distilled (Figure 8.1.1a, Appendix 1). The leaf samples were dried in an oven at 45°C during 24 h, powdered in an agate mortar (Figure 3.7c,d). Fresh grape samples were separated to the seed, pulp and skin (Figure 3.7e). All the separated samples and whole grape berries were blended. The fruit samples were frozen until a few hours before the digestion. The grapevine leaf (0.5 g), grapevine petiole (0.5 g), fresh grape berry (1 g), grapevine seed (0.5 g), grapevine pulp (1 g), grapevine skin (1 g) and moss (0.3 g) samples were digested for 45 min in a microwave digester (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy) (US EPA 3050b Method; Table 3.2.1) (Figure 3.6d) (Milićević et al., 2017b). After the digestion, all the samples were filtered through the filter paper (Filter paper, Blue Ribbon, Grade 15 (2–3 pm), Ø125 mm, producer FIORONI) and packed in the polyethylene bottles until the element concentrations measurement (Figure 3.6e,f).

For the pellet preparation of the leaf samples for the element determination by WD-XRF, the leaf samples were blended and the dry mass (5 g ± 1 mg) of the sample was mixed with wax (20% from the dry soil mass). The pellets were prepared in the press, 2 minutes on 5 bars and after 5 minutes on 15 bars. Prepared pellets were analysed on WD-XRF (Figure 3.9).

For measuring magnetic parameters for the leaf samples, approximately 0.5 g of each leaf sample was carefully packed in the clean foil and then in the polyethylene containers (volume 10 cm^3) (Figure 3.10c,d).

3.4 Instrumental analyses

3.4.1 Determination of element concentrations by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS)

The concentrations of 26 elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sr, V and Zn) in the soil samples were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6500 Duo, Thermo Scientific, UK) (Figure 3.11a). For the calibration, a Multi-Element Plasma Standard Solution 4, Specpure (Alfa Aesar GmbH & Co KG, Germany) was used. In addition, this method was used for determining 15 elements (Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr and Zn) in the grapevine leaf, petioles, grape, grape parts, wine and moss samples. The concentrations of the other eleven elements (As, Be, Bi, Cd, Co, Cr, Li, Mo, Pb, Sb and V) in the plant material (leaf, petioles, grape, grape parts, wine and moss) samples were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Scientific iCAPQ, Thermo Scientific, UK) (Figure 3.11b). In addition, 17 REEs: Ce, Dy, Er, Eu, Ga, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y and Yb in the moss samples (Experiment 4) were determined using ICP-MS (Thermo Scientific iCAPQ, Thermo Scientific, UK). The sets of the determined element concentrations for each of the experiments presented in this dissertation are presented in Table 8.1.1, Appendix 1. A low-level Elements Calibration Stock, US EPA Method Standard (VHG Labs, Manchester) was used for calibration. The different standard series were prepared separately for every procedure (Table 3.1) for calibrating the instruments. The

calibrations for the analyses were done by matrix matching method by annulling the effects of the matrix to the element determination.

Figure 3.11 a) Inductively coupled plasma-optical emission spectrometry (ICP-OES); and b) inductively coupled plasma-mass spectrometry (ICP-MS).

Table 3.2 Preview of the analytical techniques applied in the different experiments presented in this doctoral dissertation

Experiment		ICP-OES	ICP-MS	WD-XRF	SIRM	χ	Elemental C, N, H, S determination
1	soil	+	+				
	plant	+	+				+
2	soil	+	+				
	plant	+	+				
3	soil	+	+				+
	plant	+	+				
4	soil	+	+				+
	plant	+	+				
5	soil	+	+				+
	plant	+	+				
6	soil	+	+	+	+	+	
	plant	+	+	+	+	+	

3.4.2 Total element concentrations determination by dispersive X-ray fluorescence spectroscopy (WD-XRF) and determination of C, N, H and S total content

For the determination of the total element concentrations in the soil and leaf samples, non-destructive method, WD-XRF was used (Figure 3.12 b). An ARLTM PERFORM'X Sequential X-Ray Fluorescence Spectrometer (Thermo Fisher Scientific, Switzerland) was equipped with a 4.2 kW Rh X-ray tube. This equipment is able to

determine concentrations of the elements from Be to Am in the periodic table. The set of various following crystals: AX03, AX09, AX16C, PET, Ge111, LiF200 and LiF220 were used for the equipment calibration. Software ARL UniQuant was used for the quantitative sample analysis. The UniQuant program is contained of the internal standard database (UniQuant, 2015), so it can be used without previous analysis of the standard series since it is XRF program which works with the advanced Fundamental Parameters Algorithms (Beckhoff et al., 2006). For the quantitative determination of the soil and leaves element content, the method screens samples and can obtain almost all element from the periodic table if they are present in enough high concentrations to be detected by WD-XRF. For the determination of the total content of C, N, H and S in the soil samples were determined on the Vario El III CHNOS Elemental Analyser (Figure 3.12a).

3.4.3 Magnetic parameter measurements

The measurements soil χ and leaf χ of the studied samples were conducted by MS2 Magnetic Susceptibility System (Bartington Instruments Ltd., U.K.) with MS2B type dual frequency sensor, with a resolution of 2×10^{-6} SI (Figure 3.12c). The susceptibility was measured for 10 s, at the high sensitivity mode. A three-measurement procedure was carried out for background drift concentration. Before samples measurements, the instrument was calibrated with a sample containing a small ferrite bead for both high and low frequencies. The values for the samples were under the critical value for discriminating weak samples from strong ones, the correction for the air drift fluctuations was done for all the measurements and further the calculations due to removing the background drift (Dearing, 1994). The measured magnetic susceptibility was normalised by the sample mass (kg) and the polyethylene container volume (10 cm^3) due to obtaining mass-specific susceptibility value ($\times 10^{-6}$ m^3 kg^{-1}).

The determination of SIRM for studied samples was performed by the method described by Hofman et al. (2014). Previously prepared leaf samples, described in 3.3.2 Section, were magnetised with a pulsed magnetic field of 1 T with a Molspin pulse magnetiser (Molspin Ltd, UK) (Figure 3.12d,e). The magnetic intensity of the sample was measured using a Molspin Minispin magnetometer with high sensitivity ($\sim0.1\times10^{-8}$ Am^2, Molspin Ltd, UK). Each of the samples was measured twice. The instrument was

calibrated by means of a magnetically-stable rock specimen (Mitchell et al., 2010). The empty polyethylene containers were also measured as blank samples. The magnetic intensity values (mA m^{-1}), were normalised to the polyethylene container volume (10 cm^3) and to the leaf mass (g), and finally expressed in A m^2 kg^{-1}.

Figure 3.12 a) Elemental C, N, H, S Analyser; b) WD-XRF; c) Magnetic susceptibility-meter; c) magnetiser; d) magnetometer (Molspin Minispin magnetometer).

3.5 Data processing

Statistical analyses were performed using the SPSS software version 21 for Windows, Statistica 8 (StatSoft Inc., Tulsa, OK, USA), OriginPro 9.0 and R software. The normality of the data sets in all studies was tested using the Kolmogorov-Smirnov test at $p<0.05$. The Wilcoxon signed-rank test was applied for testing differences ($p<0.05$) in the element concentrations between:

- the studied grapevine varieties (*Sauvignon blanc* and *Cabernet sauvignon*−Experiments 2 and 3; and *Pannonia* and *Regent*−Experiment 5);
- soil and grapevine varieties between different vineyard parcels (Experiment 2, 3, 5);
- soil layers (Experiment 2, 3, 5);
- two studied moss species (Experiment 4); and
- exposed moss bag in different vineyard parcels (Experiment 4).

In addition, nonparametric ANOVA was used for testing the differences between:

- different parts of the grape berry (skin, pulp and seed−Experiment 2; skin, pulp, seed, leaf and petiole−Experiment 5); and
- different periods of the moss bag exposure (Experiments 4, 5).

The Spearman's correlation (R) analysis was applied to indicate

- the bioavailability i.e. relationships between the bioavailable fractions of PTEs extracted by suitable single extraction procedure from the vineyard soil (Experiments 2 and 3) and in order to assess which of the single extraction procedures is the most suitable for assessing the bioavailable PTE fraction;
- associations between the element concentrations measured in the moss bag samples (Experiment 4); and
- associations between the element concentrations in the soil and grapevine samples (Experiments 2, 3 and 5).

In addition, the Spearman's correlation (R) analysis was applied for assessing correlations between:

- pseudo-total element concentrations in the soil samples (Experiments 2, 3, 5);
- element concentrations in extracts with element concentrations in the grapevine parts − seed, pulp, skin and leaf (Experiment 2, 3);
- bioavailability risk (Experiment 2, 3);

- element concentrations in investigated moss species (Experiment 4);
- element concentrations in leaf and moss (Experiment 4);
- element concentrations measured by ICP-OES and ICP-MS, and WD-XRF in soil and leaf samples (Experiment 6);
- SIRM and χ in soil and in leaf samples (Experiment 6); and
- element concentrations and magnetic parameters in soil and leaf samples (Experiment 6).

Principal Component Analysis (PCA) with Varimax normalisation was used with the rotation method in the analysis following the standardisation of the data (Kaiser, 1958). The analysis was applied to identify:

- association between different element concentrations extracted by different extractants from the soil (Experiment 1);
- similarities between the grapevine parts and different grapevine varieties (Experiment 1); and
- the bioavailability of the potentially toxic elements and differences between the single extraction procedures for the vineyard soil (Experiments 1, 2 and 3);
- associations between the element concentrations in the soil samples and physico-chemical parameters and sampling periods (Experiment 3);
- associations between element BAC and the grapevine phases through the season (Experiment 3);
- similarities of the moss bag exposure periods in the commercial vineyard (Experiment 4);
- distinguish associations between the elements recognised as PTEs and different grapevine parts (skin, pulp, seed, petiole and leaf) of the organic grapevine (Experiment 5);
- associations between element concentrations and magnetic parameters (SIRM and χ) in the soil samples (Experiment 6);
- distinguish associations between element concentrations and SIRM in leaf samples (Experiment 6);
- associations between soil and leaf samples from the commercial and organic vineyards (Experiment 6);

- associations between magnetic parameters (SIRM and χ) in the leaf and RF (Experiment 6).

Cluster Analysis (CA) was applied to assess groups between the bioavailable element fractions of macro and micro elements from soil to different grapevine parts (Experiment 1);

Regression (R^2) analysis was used to determine associations between the calculated BGI, BAC and BRAI (Experiment 3). The Multiple correlation coefficients R (z/xy) were determined for understanding the correlations between the element concentrations in the grapevine parts (Experiment 2).

The Kohonen self-organising map (SOM) was applied in Experiment 5 as a method for the screening of the relation between the environmental implication indices between the organic and commercial (Experiments 3 and 5) vineyards. The SOM was introduced by Kohonen (1982, 1991) represents a type of neural networks method that provides a projection of multidimensional data into the nodes of a regular, usually two-dimensional grid. The SOM algorithm constructs the neurons in such a way that more similar neurons are associated with nodes that are closer in the grid, whereas less similar neurons are situated gradually further away in the grid (Kohonen, 2013). SOM has been usually applied for the investigation, clustering and visualisation in the exploration of inorganic or organic pollutants (Mari et al., 2010; Deljanin et al., 2015; Herceg Romanić et al., 2018a, 2018b) implying relations between the element concentrations. In this doctoral dissertation, it was applied to distinguish differences between environmental implications. SOM was applied, using the R software environment for statistical computing (R Team, 2012), to investigate is there any common pattern among environmental risk indices between the studied vineyards. The SOM inputs were the values (N=150–155) of each calculated index (6 in total) in the soil samples. The values of all of the used inputs were normalised to the range of 0−1. The following parameters were chosen: a number of neurons in the output layer (map) 36 (6×6), aiming for at least 5−10 samples per node when choosing map size; hexagonal grid and iterations process was optimised until the distance from each node's weights to the samples represented by that node reached a minimum plateau (Wehrens and Kruisselbrink, 2017).

3.5.1 Quality control and assurances

The blank samples and certified reference materials (CRMs) were analysed once every 10 samples. Four CRMs: Montana II Soil (2711a), Sewage Sludge-Amended Soil (BCR 143R), Contaminated Brickworks Soil (ERM CC 135a) and Soil (SARM 42) were analysed to validate the pseudo-total protocol. According to the CRMs, the recovery for pseudo-total soil analysis of the elements was ranged between 80% and 120%. For validation of the single extraction protocols, the calibrations were prepared using a low-level Elements Calibration Stock, EPA Method Standard (VHG Labs, Manchester) and for the preparation of the standard series for the calibration of every specific single extraction protocol, the matrix matching technique was applied to eliminate the problems related to the occurrence of the matrix effect during the determination of the element concentrations in the extracts. In addition, the results after the determination were selectively chosen firstly, according to Limits of the detection (LOD) of the method and secondly, according to Relative Standard Deviation (RSD<20%) of three measurements of every sample. The LOD and limits of quantification (LOQ) of the methods are given in Tables 8.1.2, 8.1.3, 8.1.4 and 8.1.5, Appendix 1. Most of the samples were analysed in triplicates and according to results for these three analysed subsamples Standard Deviation and Relative Standard Deviation (RSD range: 0.4−32%) were calculated as one of the parameters important for the validation. In addition, for the single extraction protocols validation, BCR 483 (Sewage Sludge-Amended Soil) CRM was also used. The element recoveries for elements in soil extracts are given in Table 8.1.6, Appendix 1. The recoveries of pseudo-total element content are given in Table 8.1.7, Appendix 1. For validation of the leaf, moss and grape sample protocols, the moss *Pleurozium schreberi*, MOSS2 (M2) and MOSS3 (M3), were used as CRMs (Steinnes, 1997). The recoveries are given in Table 8.1.8, Appendix 1.

3.5.2 Environmental risk assessment

The concentrations of Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Sb, V and Zn were considered for assessing the environmental and health risk in the soil or grapevine samples. According to the literature, these elements have been recognised as PTEs (US EPA, 2007). The studied elements which were not considered in the calculations still do not have any known hazardous or toxic effects.

Enrichment Factor (EF); Geochemical Index (I_{geo}), Bio-Geochemical Index (BGI), Contamination Factor (CF), Pollution Load Index (PLI), Environmental Risk (Eri and RI) and Bioavailability Risk Assessment Index (BRAI) for the soil samples were calculated (Table 3.3). BRAI was calculated for quantification of the bioavailability risk of PTEs from the vineyard soil according to the equation proposed by Jamshidi-Zanjani et al. (2015). This index was developed for element concentrations extracted by Na_2EDTA, which have probable effect levels (PEL) published by NOAA (2004) and obtained BRAI was named $BRAI_{probable}$. In this doctoral dissertation this BRAI formula was adopted but also the new one was developed using apparent effects threshold values (AET) published by NOAA (2004) for a larger elements set and this BRAI was called $BRAI_{apparent}$ (Table 3.3). Additionally, both BRAI equations were modified including the elements extracted by CH_3COOH (Experiment 3).

Bioaccumulation of the elements in the grapes' seed, pulp, skin and leaves were evaluated by calculation of biological absorption coefficient (BAC). Ratio factor (RF) of the concentrations between plant parts were estimated (Table 3.3) to assess the air influence on the outer parts of grapevine, which are directly exposed to air pollution. In addition, Limit of Quantification for moss bag technique (LOQ_T) and Relative Accumulation Factor (RAF) was calculated for moss bag samples to estimate the enrichment of PTEs in the moss material (Table 3.3).

Table 3.3 Equations for assessing environmental risk in the vineyards

Environmental risk assessment equation *soil samples*	Formula	Description	Range	References	Experiment
EF	$EF=(Cn/C_{ref})_{sample}/(Cn/C_{ref})_{background}$	Cn is the concentration of a metal element in soil and C_{ref} is the concentration of reference element	EF < 2 minimal enrichment 2 ≤ EF < 5 moderate enrichment 5 ≤ EF < 20 significant enrichment 20 ≤ EF < 40 very high enrichment EF ≥ 40 extremely high enrichment	Zhang and Liu, 2000; Chen et al., 2015	1
I_{geo}	$I_{geo}=\log_2[(C_n/1.5 \times B_n)]$	C_n is the measured concentration of the metal n, B_n is the local background concentration of metal n	$I_{geo} \leq 0$ (grade 0), unpolluted; $0 < I_{geo} \leq 1$ (grade 1), slightly polluted; $1 < I_{geo} \leq 2$ (grade 2), moderately polluted; $2< I_{geo} \leq 3$ (grade 3), moderately severely polluted; $3 < I_{geo} \leq 4$ (grade 4), severely polluted; $4< I_{geo} \leq 5$ (grade 5), severely extremely polluted; $I_{geo} > 5$ (grade 6), extremely polluted	Yaquin et al., 2008; Chen et al., 2015	1
Mobility factor	MF=Ce/Cp-t	$C_{extracted}$ / $C_{pseudo\text{-}total}$	Higher values indicate higher element mobility	Katana et al., 2013	1, 2, 3, 5
Mobility factor %	MF%= MF*100	MF is mobility factor; MF% is mobility factor expressed in %	Higher values indicate higher element mobility	Katana et al., 2013	1, 2, 3, 5
Contamination factor (CF)	$CF = Cn/Bn$	Cn is an element's concentration and Bn is the initial (control) concentration of the metal in the soil	CF≤1 low 1≤CF≤3 moderate 3≤CF≤6 considerably 6≤CF very high contamination factor	Likuku et al., 2013	1, 2, 3, 5
Pollution load index (PLI)	$PLI = (CF1 \times CF2 \times CF3 \ldots \times CFn)^{1/n}$	CF is contamination factor; n=number of determined element concentrations	PLI<1 not polluted PLI=1 baseline levels of pollution PLI>1 deterioration of site quality	Likuku et al., 2013	1, 5
Ecological risk (RI)	Eri=TR×CF RI=ΣEri	CF is contamination factor; TR is toxic response factor defined for As, Cd, Cr, Cu, Ni, Pb and Zn with known values 10, 30, 2, 5, 5, 5 and 1 respectively; Eri is the potential risk of element (i=As, Cd, Cr, Cu, Pb and Zn). RI is the sum of Eri (ΣEri)	RI≤150 low 150≤CF≤300 moderate 300≤CF≤600 acceptable 600≤CF very high	Hakason, 1980	2, 5

Biogeochemical index (BGI)	BGI= Osl/Asl BGI= Asl/Bsl	Osl-element concentration in O soil layer Asl-element concentration in A soil layer Bsl- element concentration in B soil layer	BGI>1 indicate sorption of the elements in surface or topsoil layer (O or A)	Jamshidi-Zanjani et al., 2015	3, 5
Bioavailability risk assessment index ($BRAI_{probable}$)	BRAI=ΣBdi (i=1 to n)/ΣTEi (i=1 to n)	n is the number of the PTE, TE is the toxic effect of the PTE (As, Cd, Cr, Cu, Ni, Pb and Zn) derived from the effect range median (ERM) values, calculated using probable effect levels (PEL) published by NOAA (2004).	BRAI ≤1 low risk of bioavailability 1< BRAI ≤3 medium risk of bioavailability 3< BRAI ≤5 high risk of bioavailability BRAI >5 very high risk of bioavailability	Long et al., 1995; NOAA, 2004 Jamshidi-Zanjani et al. 2015	3, 5
Bioavailability risk assessment index ($BRAI_{apparent}$)	BRAI=ΣBdi (i=1 to n)/ΣTEi (i=1 to n)	n is the number of the PTE, TE is the toxic effect of the PTE (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn) derived from the effect range median (ERM) values, calculated using probable effect levels (AET) published by NOAA (2004).	BRAI ≤1 low risk of bioavailability 1< BRAI ≤3 medium risk of bioavailability 3< BRAI ≤5 high risk of bioavailability BRAI >5 very high risk of bioavailability		3, 5
soil-leaf system					
Bioaccumulation factor (BAC)	BAC=Cp/Cs	Cp is the element concentration in different grapevine parts and Cs is the concentration of the same element in the soil sample from the same sampling site	The values BAC > 1 then the plants could be accumulators; BAC = 1 there are no influences of the soil and if the BAC < 1 means that the plant can be an excluder	Radulescu et al., 2013. Bravo et al., 2017	1, 2, 3 5
air-plant					
Ratio factor (RF)	$RF = C_{leaf}/C_{seed}$ $RF = Cl_{eaf}/C_{pulp}$ $RF = C_{skin}/C_{seed}$ $RF = C_{skin}/C_{pulp}$ $RF = C_{petiole}/C_{seed}$ $RF = C_{petiole}/C_{pulp}$	C_{leaf}- concentration in the leaf sample C_{seed}-concentration in the seed sample C_{skin}-concentration in the skin sample C_{pulp}-concentration in the pulp sample $C_{petiole}$-concentration in the petiole sample	where RF>1 indicates pollution via the atmosphere	Oliva and Mingorance, 2006	2, 5, 6
Limit of quantification for moss bag method (LOQ_T)	$LOQ_T = M + 1.96 \times SD$	M is the mean value of the initial element concentration in the unexposed moss, and SD the corresponding standard deviation		Ares et al., 2015	4, 5
Relative accumulation factor (RAF)	$RAF = (C_{exposed} - C_{initial}) / C_{initial}$		Higher values indicate higher element enrichment	Ares et al., 2015	4, 5

3.5.3 Health risk assessment

To simulate exposure of the field workers as similar to the real working conditions, it is important to set a site-specific exposure scenario, including site-specific environmental and exposure parameters, which matched the local lifestyle (Table 3.4). For indicating the health risk assessment in the vineyard studies, the worst-case scenario was observed. Among the measured elements, those that have toxicological reference values such as Reference Dose (RfD), Reference Concentration (RfC), Cancer Slope Factor (CSF), and Inhalation Unit Risk (IUR) were used for calculating health risk assessments. Applying the equations available at *The Risk Assessment Information System, RAIS* (RAIS, 2013), the potential (non-carcinogenic) and carcinogenic risks were calculated for the farmer's exposure to the soil during grapevine season: given as calculation for non-carcinogenic and carcinogenic risk assessment for outdoor workers (RAIS, 2013).

In this study, the total Cr content was determined, and a worst-case scenario of health risk assessments was calculated using the concentration of total Cr as Cr^{6+}. The estimated Daily Intake Rate (DIR), Target Hazard Quotient (THQ), Hazard Index (HI) and Target Cancer Risk (TR) values of PTEs via consumption (mg kg^{-1} day^{-1}) of the grape and wine were calculated applying the equations (RAIS, 2013). For calculation of carcinogenic risk for grapevine consumers, the adjustable formula has been used (RAIS, 2013) (Table 3.4).

Table 3.4 Equations for the health risk assessment for the field workes and the grapevine consumers

Health risk assessment	
Formula	Description
Health risk for workers	
$CDIo = \frac{C \times EF \times ED \times IR \times RBA \times CF}{AT \times BW}$	CDI_o–chronic daily intake. oral exposure (mg $kg^{-1}day^{-1}$); CDI_i –chronic daily intake. inhalation exposure (mg m^{-3}); CDI_d –chronic daily intake. dermal exposure (mg $kg^{-1}day^{-1}$); C – concentration of an element in soil (mg kg^{-1}); IR – ingestion rate (100 mg kg^{-1}); EF – exposure frequency (214 day $year^{-1}$); ED –exposure duration (35 years); RBA – relative bioavailable factor (for As is 0.6.and for other elements. it is 1); BW –body weight of workers in the vineyard (80 kg); AT –average exposuretime(365 day $year^{-1}$; 35 years for non-carcinogenic and 365 day $year^{-1}$; 70 years for carcinogenic); PEF –particulate Emission Factor ($1.4\times10^{9} m^3 kg^{-1}$); ET – exposure time (8 h day^{-1}) ; SA – surface area (3527 $cm^2 day^{-1}$); AF –adherence factor (0.12 mg cm^{-2}); ABS –fraction of contaminant absorbed dermally from soil; CF – conversion factor (1×10^{-6} kg mg^{-1}).
$CDIi = \frac{C \times EF \times ED \times ET \times \frac{1}{PEF}}{AT}$	
$CDId = \frac{C \times EF \times ED \times SA \times AF \times ABS \times CF}{AT \times BW}$	
$HQ\ o = \frac{CDI\ o}{RfD}$	
$Ro = CDI \times CSF$	
$HQ\ inh = \frac{CDI\ inh}{RfC}$	
$R\ inh = CDI \times IUR$	
$HQ\ d = \frac{CDI\ d}{RfDo \times GIABS}$	RfD – reference dose for ingestion exposure (mg $kg^{-1}day^{-1}$); RfC –reference dose for inhalation exposure (mg m^{-3}); CSF – cancer slope factor (kg day mg^{-1}); IUR – inhalation unit risk (m^3 mg^{-1}); GIABS – Gastro Intestinal Absorption Factor.
$Rd = CDI\ d \times \frac{CSF}{GIABS}$	
$HI = \Sigma HQ$	
Health risk for grape consumers	
$DIR=\frac{Mc \times I_R}{BW}$	M_C−concentration of potentially toxic elements in the fruits (mg kg^{-1}); I_R−the ingestion rate of the fruits (0.1768 kg day^{-1} for adults and 0.0681 kg day^{-1} for children); *B*W −the average adult body weight (adults 80 kg and children15 kg); EF−exposure frequency(365days $year^{-1}$); ED−exposure duration (40 for adults and 6 for children); RfD−the reference dose of individual metal (mg$kg^{-1}day^{-1}$); Atn/ATc−average exposure time for noncarcinogens/carcinogenic worst-case(365 days $year^{-1}$ ×ED); CPSo−carcinogenic potency slope oral I_{adj}
$THQ=\frac{Mc \times I_R \times EF \times ED}{RfD \times BW \times Atn}$	
$\Sigma HI=THQ1+THQ2+\ldots.+THQn$	
$CDI = \frac{C \times I_{adj} \times CF}{AT_c}$	
$I_{adj} = \frac{ED_{child} \times EF \times I_{R\ child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times EF \times I_{R\ adult}}{BW_{adult}}$	

4 Set up, specific aims and novelty of the experiments

4.1 Experiment 1: Pilot soil study in the experimental vineyard

For the first time, the extraction using deionised H_2O during 16 h was performed as an alternative single extraction procedure. In this experiment, six single extractions procedures (Table 3.1) and pseudo-total digestion were used for PTEs (major and trace elements) isolation from the vineyard topsoil (0–30 cm), sampled from nine parcels in the experimental vineyard. The aims of the experiment were to assess: i) which single extraction procedure is the most suitable for PTEs (major and trace elements) extraction from the topsoil, with special attention to the deionised H_2O 16 h, as an alternative procedure; ii) whether concentrations of major and trace elements in the soil are in a relationship with their concentrations in the grapevine parts (leaf, seed, pulp and skin); and iii) environmental implications (MF%, I_{geo} and EF) of PTEs in the vineyard soil.

4.2 Experiment 2: Bioavailability of PTEs from soil to the different grapevine parts (seed, pulp, skin and leaves) in the harvest phase; environmental implications and health risk assessment in the commercial vineyard

In this comprehensive study, six single extraction procedures were applied (Table 3.1) on the topsoil (0−30 cm) and subsoil (30−60) (A and B horisons, respectively) (Figure 2.5) from a commercial vineyard area for assessing bioavailability of the PTEs from the soil to different grapevine parts (leaf, skin, pulp and seed). The main aim of this experiment was to assess the bioavailability of PTEs from topsoil (0−30 cm, B horison) and subsoil (30−60 cm, C horison) 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 environmental implications (CF, PLI, MF%, BAC, RF) were observed in the commercial vineyard ambient (Table 3.3). According to the measured PTE concentrations, health risk implications (ΣHI and ΣR) were estimated for field workers in the vineyard, consumers of the grapevine (adults and children) and the wine (adults).

4.3 Experiment 3: An integrated approach to the investigation of temporal variations of the ambient pollution through entire grapevine season (from April to August) in the commercial vineyard

According to the available literature, there were only several studies comparing different single soil extraction procedures in a vineyard (Rao et al., 2010; Vystavna et

al., 2014; Vázquez Vázquez et al., 2016). A comprehensive study applying multivariate and correlation analyses of the calculated environmental implications indices (MF%, CF, BGI, Eri, RI, $BRAI_{probable}$, $BRAI_{apparent}$, modify $BRAI_{probable}$, modify $BRAI_{apparent}$, BAC) was performed in the commercial vineyard in Serbia with the aim of assessing the bioavailability of the target PTEs. In addition, some equations of indices such as BRAI were calculated using more comprehensive PTEs set, and the existing $BRAI_{probable}$ were compared with new developed $BRAI_{apparent}$. Moreover, for assessing the BRAI beside using concentrations of the PTEs extracted with Na_2EDTA, also concentrations extracted with CH_3COOH were used for the modify $BRAI_{probable}$ and $BRAI_{apparent}$ calculations. Specifically, the aims of this experiment were: i) to determine temporal fluctuations of environmental pollution by PTEs affecting the vineyard ambient through the entire grapevine season based on environmental implications assessment; ii) assessing the bioavailability of PTEs which showed up as pollutants of the outmost importance in the vineyard.

4.4 Experiment 4: Moss bag biomonitoring of air pollution in the commercial vineyard ambient

This experiment represents a contribution to the moss bag methodology because there was no any study before performed specifically in the vineyards, and there were only a few studies in the agricultural areas, as previously mentioned. Additionally, in this experiment the grapevine leaves investigated in the Experiments 2 and 3 were compared to the mosses in order to investigate could the grapevine leaves bioindicate air quality in the vineyard ambient. The active moss biomonitoring survey was conducted in the commercial vineyard through the whole grapevine season. Two moss species (*S. girgensohnii* and *H. cupressiforme*) were exposed in the bags for 2, 4 and 6 month periods. According to the previous studies performed in the urban area (Aničić et al., 2009c), the 2-month period should be appropriate for the reliable "signal" of the PTEs, even REEs, in the exposed mosses. However, in an agricultural (vineyard) ambient, this exposure period might be insufficient, and thus, it was of interest to test a prolonged period of the moss exposure (e.g. 4 and 6 months). Six-month bag exposure covers whole grapevine season and could be of interest for intercomparison of air pollution between different vineyards. Specifically, there were five different periods of the moss bag exposure in the vineyard: three 2-month periods (1M2: March 20^{th} – May

20^{th}; 2M2: May 20^{th} – July 20^{th}; 3M2: July 20^{th} – September 20^{th}); one 4-month (M4: March 20^{th} – July 20^{th}) and one 6-month period (M6: March 20^{th} – September 20^{th}).

4.5 Experiment 5: The first study of the PTE environmental implications in the soil-grapevine-air system performed in the organic vineyard ambient

Nowadays, organic viticulture has been increasingly fostered since it is considered to have more positive impacts on the environment and human health. The main reason for the encouragement lies in more comprehensive grapevine growth without or with minor agrochemicals application, with the possible use of compost and manure, and the lifting of trees and shrubs as a common native barrier to the penetration of possible pollutants. Thus, the aims of this experiment were to: i) estimate if the soil, the grapevine and the air in the organic vineyard are less polluted by the PTEs than in other (experimental or commercial vineyards; ii) assess which of nine applied single extraction procedures (Table 3.1) are most suitable for assessing the PTEs mobility from the soil; iii) to assess environmental and human health risks by applying various environmental implication indices and health risk assessment equations (Tables 3.3 and 3.4).

4.6 Experiment 6: Magnetic parameters as a proxy for the pollution assessment in the commercial and organic vineyards in comparison to total and pseudo-total PTE content

The goal of this experiment was to estimate could screening methods (such as WD-XRF and magnetic measurements) as cost-effective, easier and faster than destructive methods indicate the ambient pollution in the commercial and the organic vineyards. The magnetic PM of leaves (indicators for current pollution) and topsoil (indicator for the geogenic magnetic PM in soil or some historical pollution by the magnetic PM) from two vineyards were investigated. The main aim of this experiment was to assess could the magnetic parameters such as saturation isothermal remanent magnetisation (SIRM) and magnetic susceptibility (χ) be a proxy for the ambient pollution by magnetic PM and PTEs in the vineyards.

5 Results and discussion

5.1 Experiment 1: A pilot study investigating PTEs (macro and trace elements) influence on soil and grapevine

5.1.1. Single extraction procedures and pseudo-total digestion for assessing element mobility in the soil from the experimental vineyard

The acidity of the soil samples was ranged from 4.84 to 8.05 in H_2O solution and from 3.85 to 7.07 in KCl solution. It could be noticed that the soil from the experimental vineyard varied from weakly acidic to weakly alkaline. The obtained pH values in the soil samples could have an influence to the element mobility, as indicated in Table 2.2, and bioavailability and pH also could influence the PTEs toxicity to plants (Kabata-Pendias and Mukherjee, 2007; Bravo et al., 2017).

Among the tested agents, aqua regia was shown as the most aggressive among the tested agents for the element extraction which isolated the highest element concentrations from the soil (Figure 8.2.1, Appendix 2). In addition, CH_3COOH and Na_2EDTA were also proven to be aggressive extractants, which could be applied for the extraction of higher element concentrations from the soil rather than $CaCl_2$, NH_4NO_3 and deionised H_2O, (Table 8.2.1, Figure 8.2.1, Appendix 2). The acidity of CH_3COOH could enhance carbonates destruction releasing PTEs associated with carbonates and efficiently extract the mobile PTEs fraction from the soil.

For assessment the total extractable S, aqua regia and CH_3COOH were the most effective. The conditions of high pressure and acidity may influence the loss of organic S during aqua regia digestion. The concentrations of S (12–18 mg kg^{-1}) extracted by $CaCl_2$ in this experiment were comparable with corresponding studies (e.g. Hu et al., 2005). Based on the extracted concentrations of macro elements in this experiment (Figure 8.2.1, Appendix 2) and MF%, the similarity in extraction strengths was observed between $CaCl_2$ and deionised H_2O (during 16 h and 2 h). In addition, there was a similarity in capacity to extract the trace elements using deionised H_2O during 16 h and 2 h (Figure 8.2.1, Appendix 2).

The highest concentrations of the measured elements (except S) were extracted from the soil samples by pseudo-total digestion using aqua regia. The concentrations of Cu (93–118 mg kg^{-1}) and Cd (3.6–4.3 mg kg^{-1}) from this experiment were comparable with data obtained for the agricultural soils which were also treated by fertilisers and

pesticides (Pueyo et al., 2004; Meers et al., 2007; Kelepertzis et al., 2015). The pseudo-total Cu concentrations in the soil samples were higher than maximum allowable concentration (MAC) (100 mg kg^{-1}) prescribed by the national and international regulations (Official Gazette, Republic of Serbia 88/2010; EU Council Directive 86/278/EEC) (Table 8.2.1, Appendix 2). In addition, the concentration of Pb measured in the soil sample only from the parcel T6 was higher than the MAC. Higher Cu concentrations in soil could imply Cu origin from Cu-based fungicides used for treating grapevine whereas a high concentration of Pb could be explained by the proximity of the main road near the parcel T6 (Figure 8.2.1, Appendix 2).

Among the PTE concentrations measured in the soil extracts and calculated MF%, the lowest element concentrations were extracted by weak salt solutions NH_4NO_3 and $CaCl_2$ (Table 8.2.1, Figure 8.2.1, Appendix 2). The concentrations of Ni (0.02–0.27 mg kg^{-1}) and Pb (0.7–9.4 μg kg^{-1}) extracted by NH_4NO_3 (Table 8.2.1, Appendix 2) were comparable with the concentrations reported by Pinto et al. (2015). Higher K and Mn concentrations were extracted by NH_4NO_3, than by $CaCl_2$, which was also comparable with reports from some other studies (Pueyo et al., 2004). These two unbuffered weak salt solutions simulate natural soil solutions, and because of this property, they are involved in some regulations for evaluation of the ecological relevance of elements (Kabata–Pendias and Pendias, 2001). The Ni concentrations (0.02−0.27 mg kg^{-1}) extracted by $CaCl_2$ were comparable with the concentrations reported by Bakircioglu et al. (2011). Thus, weak diluted salt solutions NH_4NO_3 and $CaCl_2$ could only be used as extractants for PTEs presented in the exchangeable soil phase and water-soluble phase (Pinto et al., 2015). The concentrations of Cu (0.9–1.8 mg kg^{-1}, 4.1–27 mg kg^{-1}) extracted with deionised H_2O during 2 h in this experiment (Table 8.2.1, Appendix 2) were comparable with concentrations reported by Bakircioglu et al., (2011). In addition, the Zn concentrations (0.2–0.9 mg kg^{-1}) extracted with deionised H_2O 2 h (Table 8.2.1, Appendix 2) were comparable with concentrations reported by Niesiobedzka (2016).

Considering other applied single extraction procedures, the highest Al, Mo, Na, P, S and Si concentrations were extracted by weak acid CH_3COOH, since it is more aggressive extractant than other applied in this experiment, which could isolate PTEs from the plant rhizosphere. The chelating agent, Na_2EDTA, extracted the highest PTE concentrations of a potentially mobile fraction of soil (Cd, Co, Cu, Fe, K, Mn, Ni, Pb, V

and Zn). The concentrations of: Cd (0.03–0.16mg kg^{-1}), Cr (0.001–0.09 mg kg^{-1}), Ni (0.3–3.0 mg kg^{-1}), Pb (1.3–4.4 mg kg^{-1}) and Zn (0.8–5.3 mg kg^{-1}) measured in the soil extracts isolated by Na_2EDTA were comparable with the concentrations reported by McGrath (1996). In addition, the similar Pb concentrations (0.02–0.09 mg kg^{-1}, 1.3–4.4 mg kg^{-1}) extracted with Na_2EDTA (Table 8.2.1, Figure 8.2.1, Appendix 2) were reported by Bakircioglu et al. (2011).

In this experiment multivariate analysis was applied to obtain PTEs association in different soil extracts (Figure 5.5.1). According to the PCA, the significant ($p<0.05$) element associations could indicate their common agro-chemical origin, but also similar plant uptake mechanism from the soil (Kabata–Pendias & Pendias, 2001; Buccolieri et al., 2010; Vystavna et al., 2015). The most significant association ($p<0.05$) was obtained between Cu, S and Zn concentrations in deionised H_2O 16 h soil extract (Figure 5.1.1b). Applying Na_2EDTA and CH_3COOH single extraction procedures, the significant ($p<0.05$) associations were obtained between Cu and Zn concentrations in the soil extracts (Figure 5.1.1e,f). Between Cu and S concentrations extracted with deionised H_2O 16 h, $CaCl_2$ and NH_4NO_3 the significant ($p<0.05$) associations were also established (Figure 5.1.1b,c,d). These elements could enter through the soil surface layer (O horison) (Figure 2.5), while grapevines were foliar treated with fungicide, Cu(II)-sulphate. In addition, the S concentrations, extracted with deionised H_2O during 16 h, were associated with Mn and Na concentrations. The associations between these elements point to their origin from the fertilisers or pesticides which are usually applied in an agriculture production (Kabata–Pendias and Pendias, 2001). Contrary, not observed any associations between Cu concentration and the other elements in soil extract after 2 h deionised H_2O extraction indicate that 2 h was probably not enough for this soil type to obtain the balance between solubility and sorption on the substrate matrix.

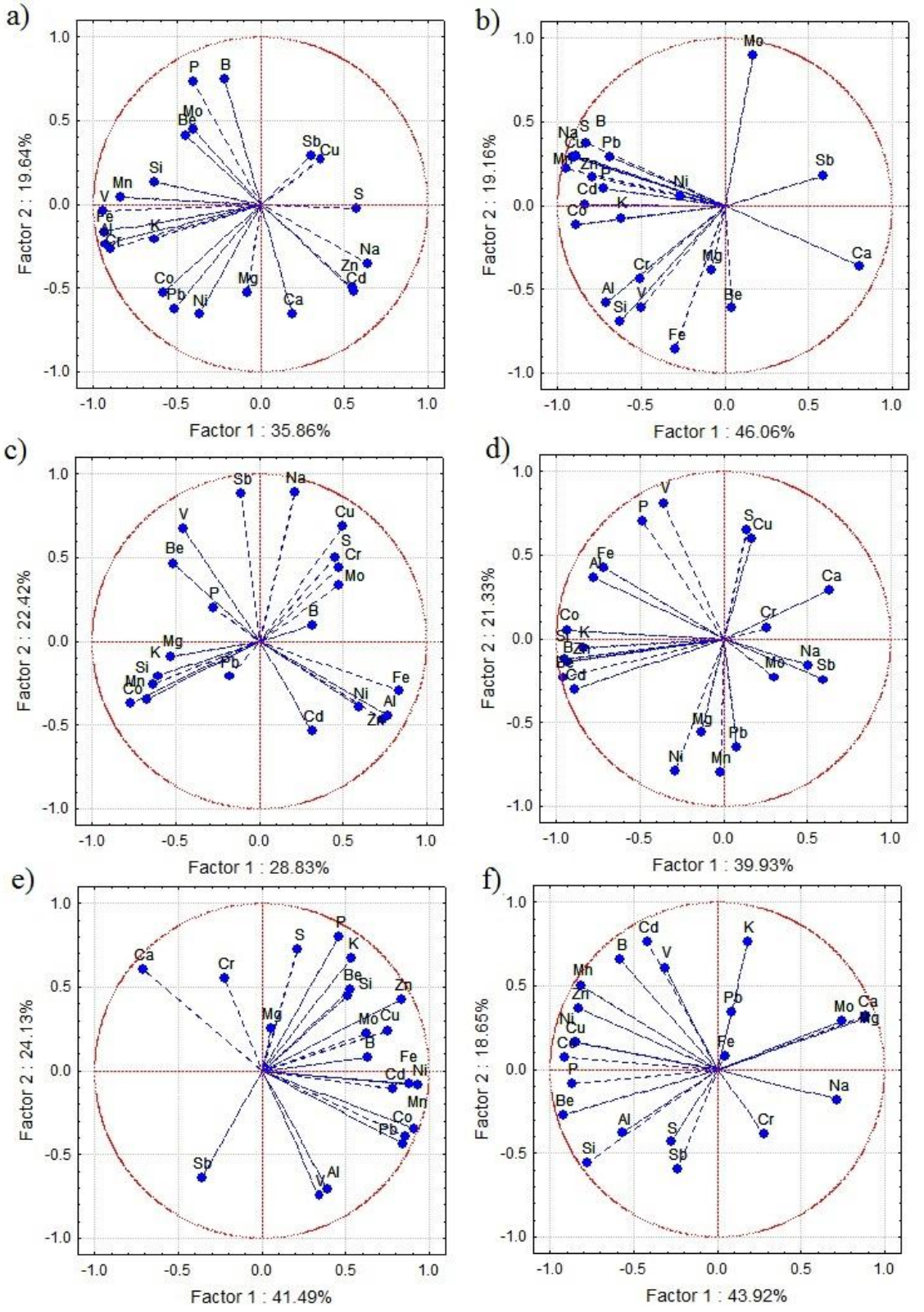


Figure 5.1.1 PCA between the element concentrations (mg kg^{-1}) extracted by; a) 2 h H_2O; b) 16 h H_2O; c) $CaCl_2$; d) NH_4NO_3; e) Na_2EDTA and f) CH_3COOH single-extraction procedures (adopted and modify from Milićević et al., 2017a).

5.1.2 Plant–soil system: assessment of the most suitable single extraction procedure for extracting bioavailable PTEs (macro- and micro elements) from the vineyard soil

Observing the measured PTE concentrations in the investigated grapevine parts (seed, pulp, skin and leaf), the highest concentrations of Cd, Cr, Cu, Ni, Pb and Zn were observed in the grapevine leaf samples (Table 8.2.2, Appendix 2). One of the most important nutrients, K, which is essential for grapevine growth, was measured in the highest concentrations among the measured element concentrations in all grapevine parts. The highest Ni concentration (52 mg kg^{-1}) was measured in the skin of *Prokupac* variety, planted on the parcel T4 that is located 1.5 km away from the waste disposal area of Institute of Nuclear Science "Vinča" (*personal communication*, 2014) (Figure 3.2). Contrary, much lower Ni concentration (0.12 mg kg^{-1}) was obtained in *Cabernet sauvignon* skin collected from the same parcel T4. The concentrations of Ni in all grapevine parts and varieties varied from 0.41 to 1.44 mg kg^{-1} with the exception of the concentration in *Prokupac* skin (Table 8.2.2, Appendix 2). Finally, Ni concentrations in all grapevine parts were below the range of excessive or toxic levels, which in the most plant varieties vary from 10 to 1000 mg kg^{-1} (Kabata – Pendias and Mukherjee, 2007). The Cu concentrations in the grapevine leaf samples ranged from 29 to 170 mg kg^{-1} (Table 8.2.2, Appendix 2). In all investigated grapevine parts, Pb concentrations were low (Table 8.2.2, Appendix 2). Low Pb concentrations were especially measured in the leaf (0.02 mg kg^{-1}) and the seed (0.02 mg kg^{-1}) of *Cabernet franc*, planted on the parcel T6 while its concentration in soil was very high 226 mg kg^{-1}. From the soil, Pb can only passively be adsorbed by the roots (Kabata- Pendias and Mukherjee, 2007), and thus, its plant uptake from the soil is generally very low (Table 8.2.2, Appendix 2). Finally, it seems that this variety is not hyper-accumulator of PTEs from the soil.

Similarities among PTE concentrations measured in the seed, pulp, skin and leaf were observed using PCA. Plot scores 1 and 2 were isolated and the leaf samples of all varieties were grouped (Figure 5.1.2), except *Prokupac* variety. The skin (PS) and leaf (PL) samples of *Prokupac* variety were distant from the skin and leaf samples of the other investigated varieties (Figure 5.1.2). *Prokupac* is grown on the parcel T4. Thus, the air-exposed grapevine parts (e.g. leaves and skin) in this parcel, distinguish from other parts probably because of the higher influence of Ni concentrations. Thus, the air-exposed Prokupac parts could indicate the influence of some PTEs from the air.

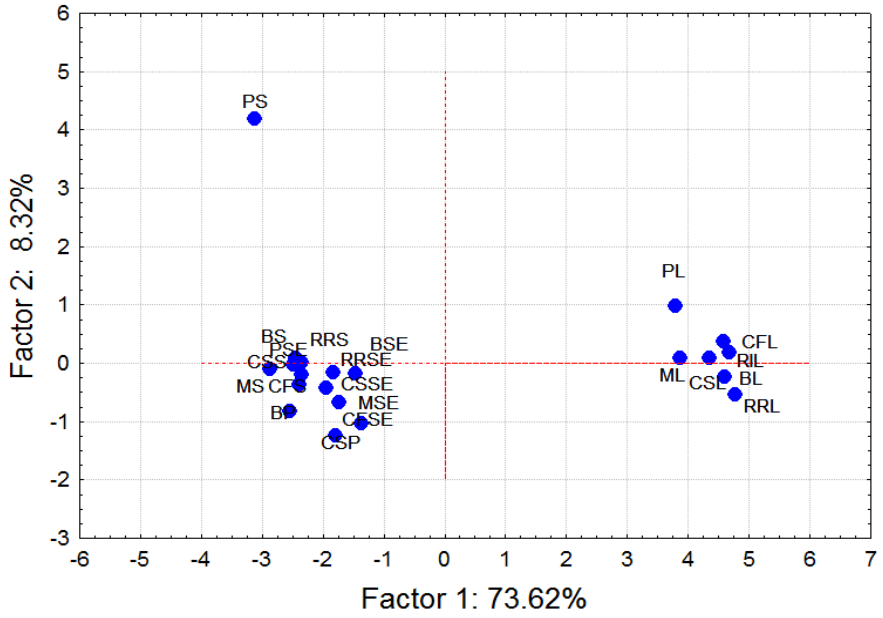


Figure 5.1.2 PCA analysis of element concentrations (mg kg^{-1}) in the grapevine parts of seven investigated varieties (adopted and modify from Milićević et al., 2017a).

The bioavailable major elements fraction (Al, Fe and K) extracted from the soil using CH_3COOH, $CaCl_2$, NH_4NO_3, Na_2EDTA, deionised H_2O 2 h and 16 h were separated as the individual cluster (Figure 5.1.3a). Moreover, according to the high Euclidian distances, the aqua regia was distinguished from all other investigated extractants (Figure 5.1.3a), probably because it isolated the highest pseudo-total element concentrations from the soil. Deionised H_2O extracted bioavailable trace element concentrations which were significantly ($p<0.05$) grouped with trace element concentrations in the grape seed and the grape pulp (Figure 5.1.3b). The weak salt solutions $CaCl_2$ and NH_4NO_3, complexing agent Na_2EDTA and weak acid solution CH_3COOH, enabled the extraction of trace elements from the soil which were in relation with trace elements in the grape skin (Figure 5.1.3b). Finally, according to the obtained dendrogram, the aqua regia showed as efficiently agent for isolating the trace element concentrations that associate with trace element concentrations measured in the grapevine leaves (Figure 5.1.3b). Thus, bioavailable element fractions have an influence on the trace element concentrations in the grape seed and pulp (inner grapevine parts), but not in leaves because these elements in the leaves could originate both from air deposition and be uptaken from the soil.

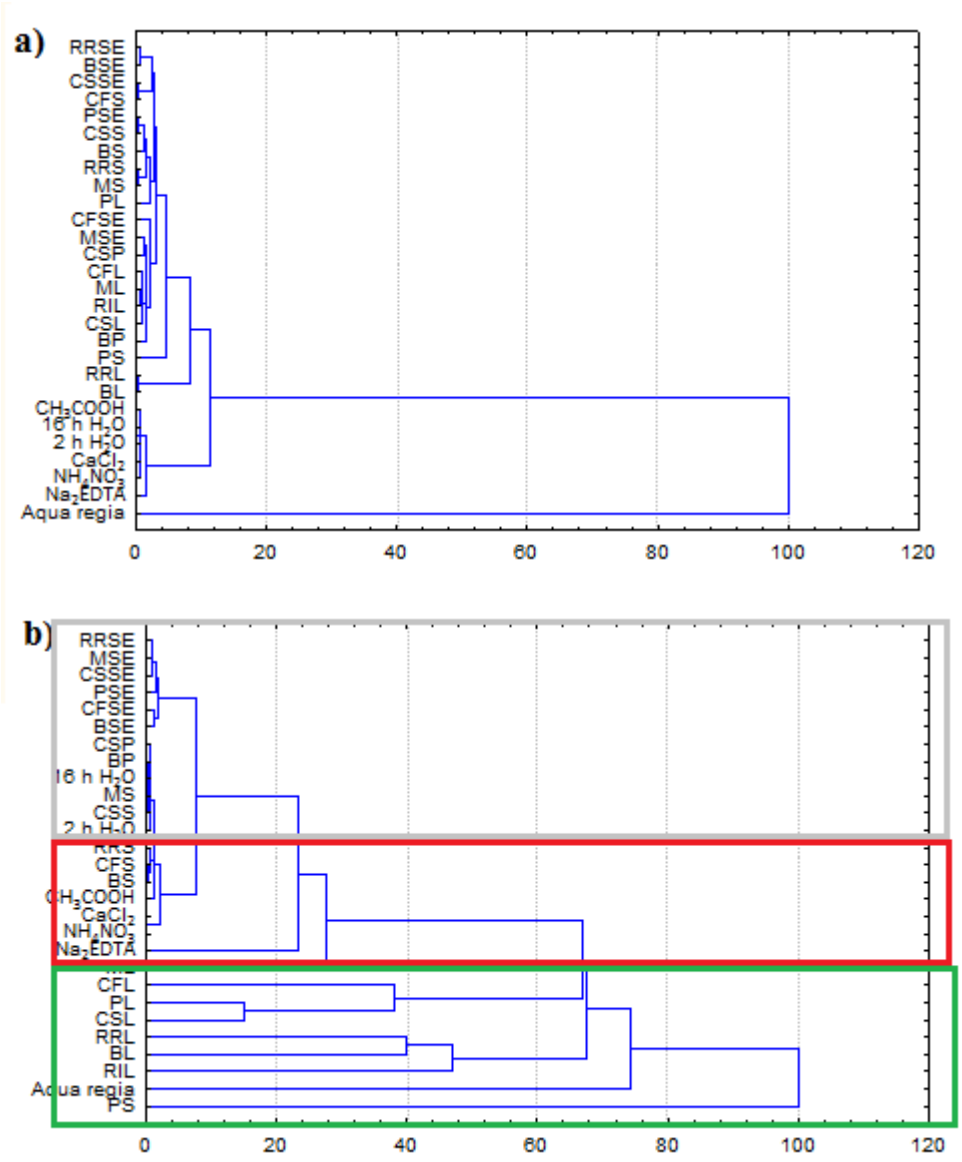


Figure 5.1.3 The clusters of bioavailable a) major and b) trace element concentrations (mg kg^{-1}) extracted by different extractants from soil and concentrations obtained in grapevine parts (abbreviations are presented in *Table 8.2.2, Appendix 2) (grey circled cluster represents the association between elements extracted from soil by H_2O and obtained concentrations in seed; red circled cluster represents the association between elements extracted from soil by weak salt, solutions, weak acid and chelating agent with obtained concentrations in pulp and skin; and red circled cluster represents the association between pseudo-total element concentrations in soil with those concentrations obtained in leaves) (adopted and modify from Milićević et al., 2017a).

5.1.3 Environmental implications assessment in the experimental vineyard

5.1.3.1 Soil

The obtained CF values showed that the concentrations of Zn in the soil samples collected from the parcels T4 and T5 were referred to moderate contaminated (CF>1), and from the parcel T6, CF for Pb was significantly higher than 1 (27.3) (Table 8.2.3, Appendix 2). Thus, CF for T6 parcel indicates very high soil contamination (CF>6) (Matong et al, 2016). The higher CF could be explained by the pollution originating from traffic activities from the nearby main road. In addition, increased CF values (Table 8.2.3, Appendix 2) obtained for the soil from parcels T4 (Cd, Co, Cu, Zn) and T5 (Cd, Co, Cr, Cu, Mo, V, Zn), could be a consequence of the influence of air pollutant deposition originating from the waste disposal area of Institute of nuclear research "Vinča" (*personal communication*, 2014). Finally, the calculated PLI values slightly higher than 1 were only obtained for the parcel T6 (Figure 3.2) (PLI=1.16) (Table 8.2.3, Appendix 2).

According to obtained I_{geo} for soil in the parcel T6 for Pb was in grade 5 (4.2), that indicated the parcel T6 as severely to extremely polluted. Observing the EF values (using Al as soil background element), the most obtained EF values were ranged 1<EF<2. According to EFs, it could be noticed that for most of the investigated parcels enrichment values were minimal to moderate, except EF calculated for Pb in the parcel T6 (Table 8.2.4, Appendix 2). Thus, there were probably the strong Pb anthropogenic influences on the soil. In addition, there was also the influence of Ni concentration on the parcel T6 and influence of Zn concentration to the parcel T4 (Table 8.2.4, Appendix 2).

All the above calculated and explained environmental implication indices imply that only for the parcel T6 there were high environmental pollution implications caused by PTEs (mostly Pb) and moderate environmental implications were identified for the parcels T4, T5, T10 and P (Figure 3.2) (Table 8.2.3, 8.2.4, Appendix 2).

5.1.3.2 Grapevine

The obtained BAC of Al, Cd, Cr, Cu, Fe, K, Ni, Pb and Zn for all investigated grapevine parts were calculated (Table 8.2.5, Appendix 2). According to the calculated BAC values, it could be noticed that the leaves of *Riesling rain* (1.77), *Riesling italian* (1.66), *Cabernet sauvignon* (1.36) and *Cabernet franc* (1.38; 1.82) could be considered as potential Zn accumulators from the soil. In addition, the leaves of *Riesling rain* (1.19), *Burgundy* (1.02) and *Riesling italian* (1.66) could be observed an accumulator of Cu from the soil. The skin of variety *Prokupac* (4.89) was shown as a markedly plant accumulator of Ni from the soil (Table 8.2.5, Appendix 2).

The results from Experiment 1 have been published in the international journal *Chemosphere* (Manuscript: *Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion*; Milićević et al., 2017a). After this pilot experiment, the extension of the investigation of mobility and bioavailability specifically for each measured element from soil to different grapevine parts (seed, pulp, skin and leaf) were assessed in the commercial vineyard during the grapevine harvest, and also the whole berries and wine prepared from these grape berries were analysed. In addition, the comprehensive assessment of the environmental and health risk in the commercial vineyard was done by combining various equations for environmental risk assessment and equations available at *The Risk Assessment Information System, RAIS* (RAIS, 2013) for human (field workers and grapevine and wine consumers) health risk assessment.

5.2 Experiment 2: Bioavailability of PTEs in the soil–grapevine (leaf, skin, pulp and seed) system accompanied by environmental implications and health risk assessment in the commercial vineyard

5.2.1 Element concentrations in the soil−grapevine system

5.2.1.1 PTE concentrations in the soil

The elements highlighted as PTEs (listed in the section 3.5.2: Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Sb, V and Zn) for plants and humans are of the major interest for bioavailability studies (US EPA, 2007), and that set of the PTEs will be further discussed with special attention. For a better understanding, the bioavailability phenomenon regarding PTEs, the soil physicochemical parameters were measured in the studied samples. Across the vineyard parcels, the acidity of the soil samples ranged from 7.06 to 7.88 (pH H_2O), from 6.33 to 6.92 (pH KCl) and from 6.53 to 7.06 (pH $CaCl_2$). The analysed soil samples were low–acid to neutral and with low soil organic matter (OM) content (ranged from 0.48% to 0.95%) that is in accordance with the allegations published by Ninkov et al. (2014). The vineyard soil was alluvial colluvial (Coluvic Regosol), very carbonated, sandy clay and poorly humus soil (Ninkov et al., 2014).

Between the studied vineyard parcels, the element concentrations in the soil did not significantly ($p<0.05$) vary. Unlike, according to the Wilcoxon test, there were statistically significant ($p<0.05$) differences between the topsoil (A horison) and subsoil (B horison) layers for Al, As, Ba, Cd, Cr, Cu, K, Li, Ni, Pb, Sb, Sr and V concentrations (Figure 5.2.1), but not for B, Be, Ca, Co, Fe, Mg, Mn, Na and Zn concentrations. For the PTEs that showed significant difference between the soil layers, the bioavailability to the grapevine parts was considered separately for both layers (A and B).

In the national and international regulations prescribed for the soil, the MACs are prescribed only for a non-comprehensive set of PTEs (As, B, Cd, Cr, Cu, Ni, Pb and Zn). The investigated vineyard soil was prominently polluted by Cd, Cr and Ni concentrations (Table 8.3.1, Appendix 3; Figure 5.2.1). The Cr and Ni concentrations were above the MAC (Official Gazette, Republic of Serbia 88/2010) in both the topsoil and the subsoil samples (Table 8.3.1, Appendix 3; Figure 5.2.1). Chromium and Ni usually originate from the parent substrate (C horison) on which the soil was formed (Figure 2.5). According to the Geochemical Atlas of Europe (Salminen et al., 2005),

there are naturally elevated concentrations of Cr and Ni in the soil of the Balkan Peninsula. However, in the topsoil samples, the concentrations of Cr and Ni did not have any significant correlation with the Fe concentration, which is a typical geogenic constituent. Otherwise, in the subsoil samples, a significant correlation was observed between Fe and Cr concentrations (Table 8.3.2, Appendix 3). Generally, Cr mobility in soil depends on the sorption characteristics which strongly dependent on iron (hydro)oxide content, supported with an adequate pH value and OM content in the soil (Wuana and Okieimen, 2011). Chromium is a generally low mobile element, especially under moderately oxidising and reducing conditions and near-neutral pH values (Kabata–Pendias and Mukherjee, 2007). Accordingly, in the studied vineyard topsoil, with near-neutral pH, low OM and the absence of any correlation with Fe concentration, the Cr concentration could originate from the agrochemicals (e.g. phosphate fertilisers or pesticides) or the proximity of anthropogenic sources (foundry or traffic activities) (Kabata–Pendias and Mukherjee, 2007). The concentrations of Cr in this study were several times higher in comparison to the Cr concentrations measured in the local background soil sample, and also the concentration was multiple higher than Cr measured in the vineyard soil in Spain (3.13–4.94 mg kg^{-1}), reported by Vázquez Vázquez et al. (2016). Beside the high concentrations of Cr and Ni in the studied topsoil and subsoil could be caused by certain (dominant) portion of the elements originated by geogenic background and certain portion originated from anthropogenic pollution (agrochemicals or surrounding foundry). Correlations between Cr and Ni concentrations in the topsoil and in the subsoil were very high (R=0.94; R=0.87, respectively, $p<0.01$; Table 8.3.2, Appendix 3) that could indicate that these elements probably originate from the same source or show similar behaviour in the soil.

In the topsoil, obtained Cd concentrations were higher than the MAC (Official Gazette, Republic of Serbia 88/2010), unlike the concentrations measured in the subsoil (Figure 5.2.1). As it is well known, Cd is one of the most toxic elements which could affect all biological processes in humans, animals and plants, as well as food quality. It could originate from P-fertiliser application, which can cause multiple increases of the Cd concentration in the agricultural soils (Kabata–Pendias and Mukherjee, 2007).

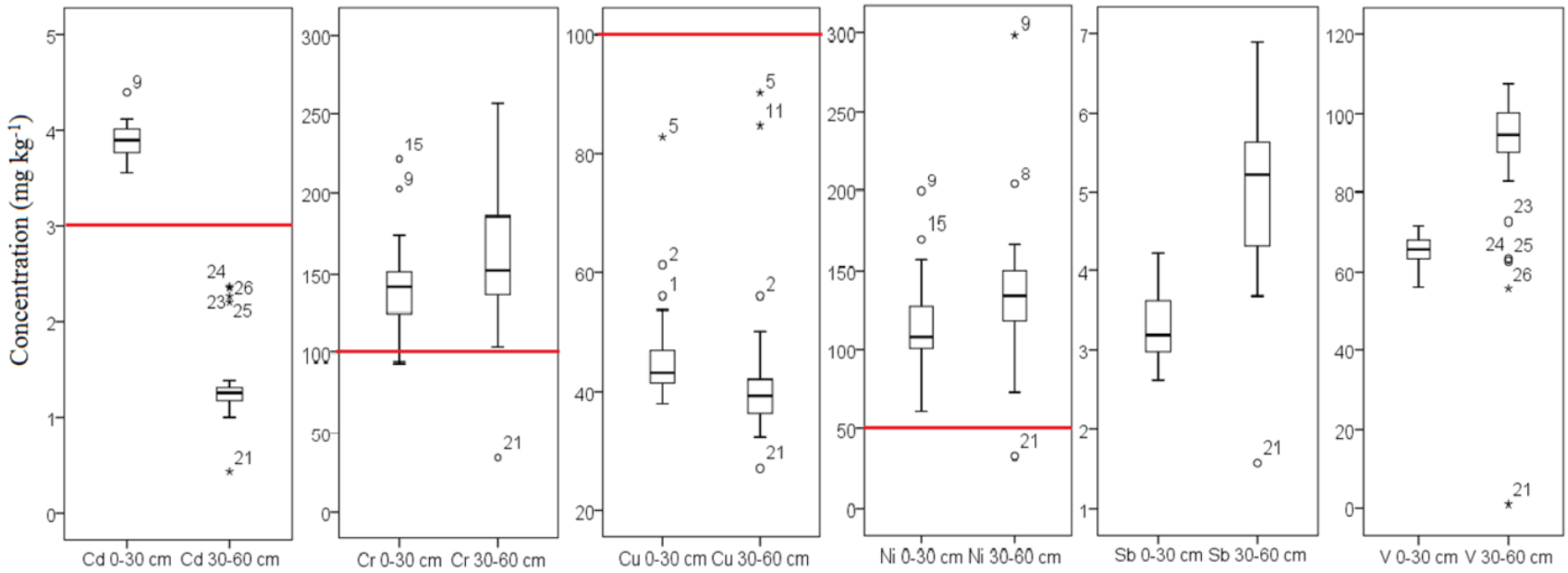


Figure 5.2.1 The concentrations (mg kg^{-1}) of PTEs in the topsoil (0–30 cm) and subsoil (30–60 cm) layers, the red lines represent MAC (mg kg^{-1}) for elements in the soil prescribed by the Official Gazette of Republic of Serbia; the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of measured concentrations; "°" represent outliers and "*" represent extremes (Milićević et al., 2018a).

The soils in vineyards are commonly polluted by Cu, sometimes up to several times higher than the MAC, because of the historically frequent application of Cu-based fungicides (Duplay et al., 2014). Surprisingly, the concentrations of Cu in the soil were lower than the MAC (Official Gazette, Republic of Serbia 88/2010) in the investigated commercial vineyard. Moreover, the concentrations of Cu (0−30 cm: 38−83 mg kg^{-1}; 30−60 cm: 27−90 mg kg^{-1}) obtained in the investigated soil were in the same range as those obtained in Experiment 1 (93–118 mg kg^{-1}) conducted in an experimental vineyard (Milićević et al., 2017a). However, Cu concentrations in the topsoil in this experiment were higher than the concentrations recently reported for the vineyards in Ukraine (Cu: 25 mg kg^{-1}) (Vystavna et al., 2014). In the subsoil, the Cu and Zn concentrations significantly correlated (R=0.48, $p<0.05$; Table 8.3.2, Appendix 3) while there was no observed correlation between their concentrations in the topsoil. This significant ($p<0.05$) correlation between Cu and Zn can be confirmed by the hypothesis that Cu and Zn originate from the same source (the frequent application of agrochemicals) reported by Komárek et al. (2010) or can be confirmed by their historical accumulation in deeper soil layer.

Observing the obtained concentrations, Sb and V concentrations were higher in the subsoil than in the topsoil (Table 8.3.1, Appendix 3; Figure 5.2.1). In the both studied soil layers (A and B), the concentration of V was strongly correlated with Al concentration (0−30 cm: R=0.85, $p<0.01$; 30−60 cm: R=0.63, $p<0.01$; Table 8.3.2, Appendix 3). Aluminosilicates and Al and Fe (hydro)oxides represent the soil constituents of the major importance for V mobility and bioavailability from soil (Larsson et al., 2013), so it seems that V in investigated soil in this experiment had mostly a geogenic origin. The Sb concentration was significantly correlated with the concentrations of B, Cr and Ni in both investigated soil layers, while in the subsoil, Sb was correlated with Al and Fe concentrations (Table 8.3.2, Appendix 3). Thus, the significant correlations imply that in topsoil Sb could mostly originate from the anthropogenic sources and in the subsoil, the significant correlations indicated Sb attachment to Al and Fe (Kabata–Pendias and Mukherjee, 2007), which probably suggest its geogenic origin in the subsoil. It should be noted that the commercial vineyard is formed on the no-till grapevine growing system (*personal communication*,

2015), and higher concentrations of some PTEs in the subsoil could be caused by the leaching of some labile-bound elements from the topsoil.

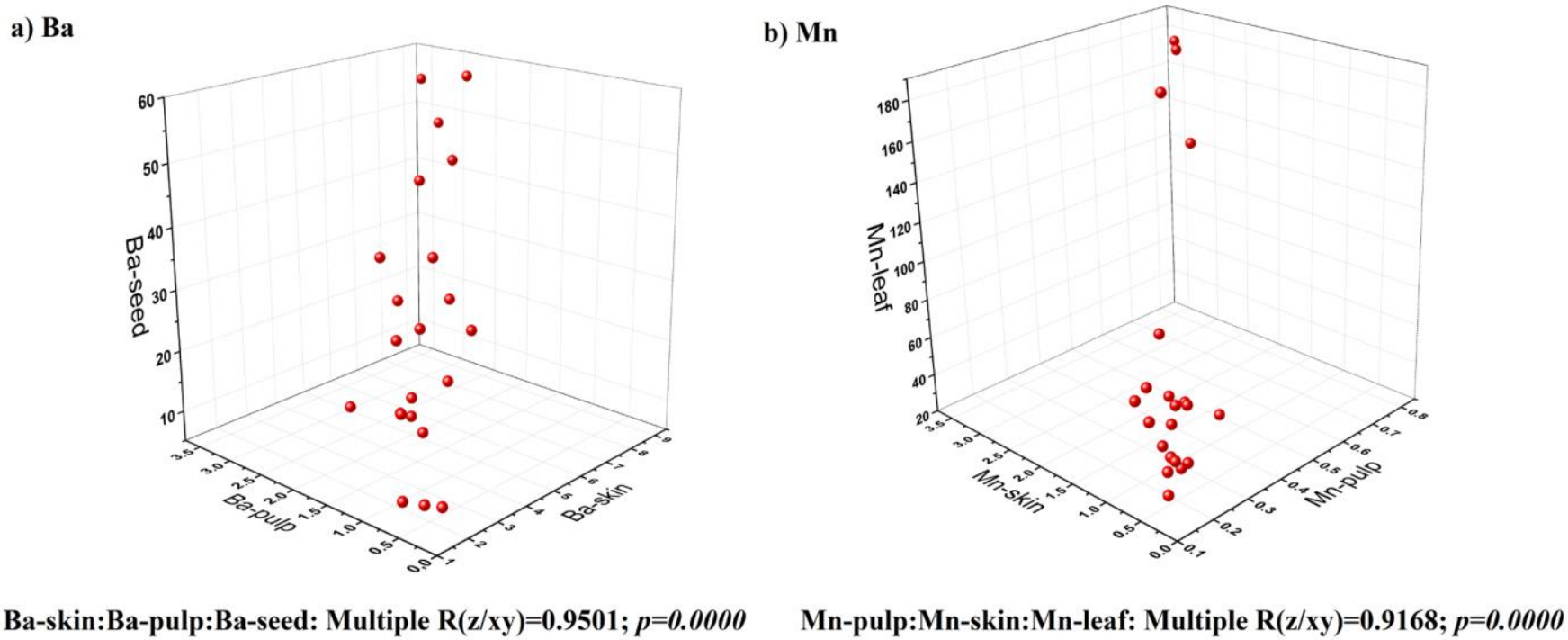
All investigated extractants in this experiment (Table 3.1) could not be appropriate and selective for isolating all bioavailable PTEs from topsoil and subsoil. According to calculated MF% for PTEs in soil extracts, the highest percentage of Al, As, Ca, Cd, Co, Cu, Fe, K, Mn, Pb, V and Zn extracted using Na_2EDTA (Table 8.3.1, Appendix 3) were observed from the soil in the harvest period. The chelating agent Na_2EDTA represents effective and selective extractant for isolating the PTEs with which it usually can build very stable complexes (Inczédy, 1976). Furthermore, the weak acid solution CH_3COOH isolated the highest concentration of B, Be, Cr, Li and Ni, probably these PTEs were bound to carbonates in the soil samples, on which the extractant acidity had an influence. Weak salt solution NH_4NO_3 extracted the highest Ba and Sr content (Table 8.3.1, Appendix 3) from the soil, probably because of NH_4^+ ion bind complexes with Ba and Sr from the soil (Hooda, 2010). The MF% of PTE concentrations in soil extract by deionised H_2O and $CaCl_2$ were low (Table 8.3.1, Appendix 3).

5.2.1.2 PTE concentrations in grapevine and wine

The PTEs in the grapevine samples (leaves and grape berries) did not vary significantly ($p<0.05$) between the investigated parcels and the grapevine varieties investigated in this experiment. The differences between the grapevine varieties were probably not observed because *Cabernet sauvignon* is the progeny variety of the *Sauvignon blanc* (Bowers and Meredith, 1997). The MAC only for few PTEs in fruits (grape) is prescribed by the national regulations (Official Gazette, Republic of Serbia 5/92, 11/92). Hence, the PTEs concentrations (As, Cd and Pb) in the studied grape berries (Table 8.3.3, Appendix 3) were obtained in lower concentrations than the MAC (Official Gazette, Republic of Serbia 5/92, 11/92). Overall, the observed contamination of the soil by Cd, Cr and Ni had no influence on the grapes, because their concentrations in the grapevine parts were low (Table 8.3.2, Appendix 3). The low uptake and accumulation of the PTEs in the grapevine was probably a consequence of neutral pH and low content of OM in the soil, which did not accelerate the PTEs desorption from the soil (Kabata–Pendias and Mukherjee, 2007).

Additionally, observing the scatter plots (the multiple correlation coefficients – R), only Ba and Mn showed a significant positive mutual correlation among the concentrations of the analysed grapevine parts (seed, pulp, skin and leaf) (Ba_{skin}–Ba_{pulp}–Ba_{leaf}: Multiple R(z/xy)=0.86, *p=0.00*; Ba_{skin}–Ba_{pulp}–Ba_{seed}: Multiple R(z/xy)=0.96, *p=0.00*; Mn_{seed}–Mn_{pulp}–Mn_{skin}: Multiple R(z/xy)=0.87, *p=0.00*, and Mn_{skin}–Mn_{pulp}–Mn_{leaf}: Multiple R(z/xy)=0.92, *p=0.00*) (Figure 5.2.2). Higher correlations between Mn concentrations were obtained within the outer parts of the grapevine, such as the leaves and the skin, than in the pulp samples. Conversely, the higher correlations were obtained between Ba concentrations within the inner berry parts such as the seed and the pulp, and than in the skin. Thus, the different multiple correlation R(z/xy) coefficients indicate that these elements could have a different origin. Barium mostly originated from the soil while Mn mostly originated from the air deposition caused by the foliar application of Mn-pesticides (in this vineyard Maneb was frequently used during the grapevine season−information by viticulturist; *personal communication*, 2015).

According to the national and international regulations (Official Gazette, Republic of Serbia 5/92, 11/92; Plotka-Wasylka et al., 2017), the PTE concentrations in the wine samples were not obtained above the MAC (Table 8.3.3, Appendix 3). Still, in the wine samples, Al and Fe were observed in higher concentrations than the MAC (Figure 5.2.3). In the white wine sample, Ni was not detected (<DL), while in the red wine measure concentration of Ni (0.7 mg L^{-1}) was slightly higher than MAC (0.1 mg L^{-1}). The higher Al, Fe and Na concentrations in the wine samples may influence the wine organoleptic peculiarities, commonly referred to as “minerality” (Laurie et al., 2010).



Ba-skin:Ba-pulp:Ba-seed: Multiple R(z/xy)=0.9501; *p=0.0000*

Mn-pulp:Mn-skin:Mn-leaf: Multiple R(z/xy)=0.9168; *p=0.0000*

Figure 5.2.2 3D graph with the equation of the multiple correlations between the concentrations (mg kg^{-1}) of a) Ba in the inner grapevine parts and b) Mn in the outer grapevine parts (Milićević et al., 2018a).

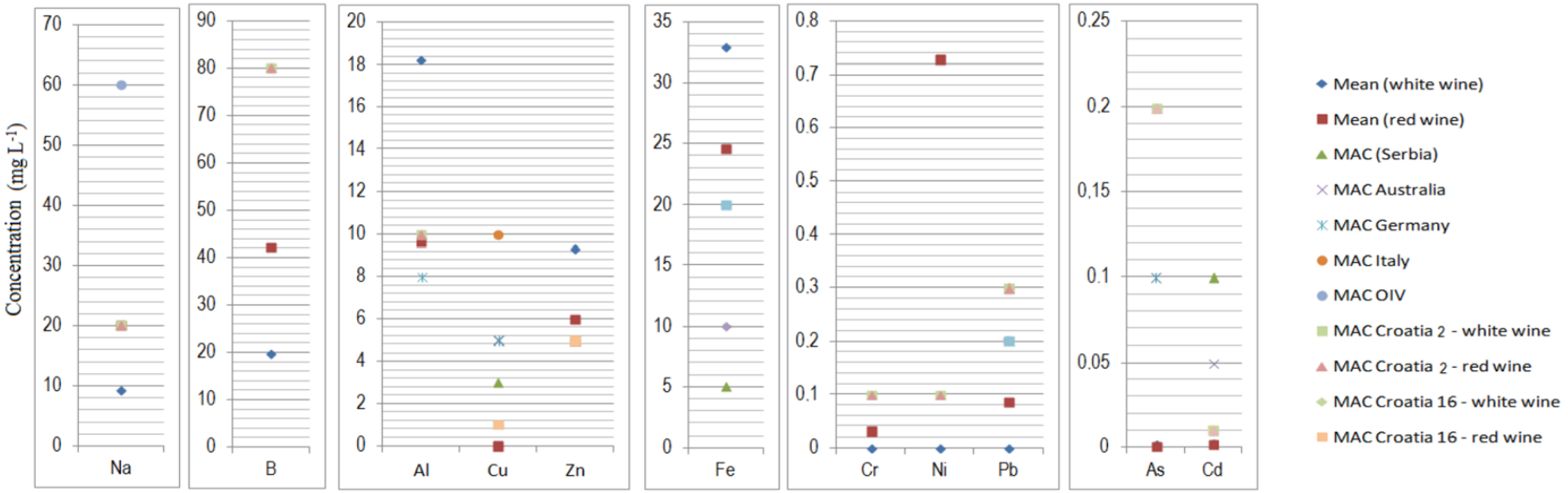


Figure 5.2.3 Concentrations (mg L^{-1}) of PTEs in the wine samples; MAC–maximum allowable concentrations (mg L^{-1}) of the elements for wine prescribed by the regulations in different countries (Milićević et al., 2018a).

5.2.1.3 Assessment of PTE bioavailability from topsoil (0−30 cm; A horison) to the grapevine parts (seed, pulp, skin and leaf)

Differently extractable PTE concentrations from the soil had a specific significant positive intercorrelation with PTE measured in the different grapevine parts, which will be further discussed in conjunction with the obtained soil physicochemical parameters. Multivariate analyses (in parallel PCA and correlation) were performed between the concentrations of the PTEs obtained in the soils and the PTE concentrations obtained in the grapevine parts (Table 8.3.4, Appendix 3).

Topsoil versus grapevine leaf. Observing the PCA and correlation coefficients (R), the most suitable extractants for isolating bioavailable Mn and Ni concentrations from the topsoil to the leaf were the weak salt solutions $CaCl_2$ and NH_4NO_3 (Figure 5.2.4c,d; Table 8.3.4, Appendix 3), and the most appropriate for Be extraction was only NH_4NO_3 (Table 8.3.4, Appendix 3). Chelating agent Na_2EDTA showed as an appropriate extractant for obtaining the correlation between Cu and V concentrations from the topsoil and the leaf (Figure 5.2b,e; Table 8.3.4, Appendix 3); and for extracting bioavailable Ba concentrations, all studied extractants were suitable (R=0.57−0.75, $p<0.01$; Table 8.4.4, Appendix 5). Mobility and bioavailability of some of the elements (e.g., Be, Mn and Ni) are strongly regulated by the soil pH, those elements could be easily mobile under the low acid to neutral soil pH (Table 2.2; Kabata–Pendias and Mukherjee, 2007), which was obtained in the studied soil. The Cu concentration in the soil depends on the vineyard age (the studied vineyard in this experiment were five to seven years old at the moment when the experiment was performed−information from viticulturists*; personal communication*, 2015). Copper is frequent monitored PTE in the vineyard ambients because of the long-term use of the parcels for viticulture which could cause high Cu accumulation in the soil (Komárek et al., 2010; Thomas et al, 2012), and also its accumulation in the grapevine parts, but in parallel accumulation of airborne Cu in the leaves could be caused by the foliar application of Cu-fungicides. As previously explained, V in the soil seems to be associated with Fe in the topsoil samples (Table 8.3.2, Appendix 3), and chelating agent probably simulated the natural processes in the soil-plant system by exchangeability of the ions and their uptake by the root system. It is known that plants can uptake Ba quite easily from acid (Kabata–Pendias

and Mukherjee, 2007) and probably weak acid soils, which was characteristic for the investigated soil.

Topsoil versus grape skin. The most significant correlations suggested that the most suitable extractant for isolating bioavailable Cu and Zn from the topsoil (Figure 5.2.4b,f; Table 8.3.4, Appendix 3) which were bioavailable to the grape skin was Na_2EDTA, as was the case for Cu with a concentration that significantly correlated with the concentration in the leaf (Figure 5.2.4b). As it was observed in Experiment 1, the significant ($p<0.05$) association between Cu and Zn (Figure 5.1.5e) imply their origin from the application of the pesticides. In this case, Cu and Zn in the grapevine skin could originate from the pesticides, because these elements originating from the same source could be deposed on the soil surface and on the air-exposed grapevine parts (e.g., skin). Because Cu is generally slightly mobile in plants as it is strongly bound to nitrogen and proteins (Komárek et al., 2010), the direct accumulation Cu from the surface of the leaves is more reliable than its accumulation from the soil.

For obtaining Mn concentration from topsoil, which correlated with its concentration in the skin (Figure 5.2.4c; Table 8.3.4, Appendix 3) NH_4NO_3 was the most appropriate single extractant, as it was also observed for Mn in the leaf. In addition, for Fe and V concentrations extraction, which were in correlation with their concentrations in the skin, deionised H_2O 16 h was suitable (Figure 5.2.4e; Table 8.3.4, Appendix 3). The concentration of Ba in the skin was significantly correlated with its concentration extracted from the topsoil using all the tested extractants (R=0.53−0.90, $p<0.01$; Table 8.3.4, Appendix 3). Unbuffered week salt solutions, $CaCl_2$ and NH_4NO_3 effectively simulate the natural soil solutions and only can extract the elements from the exchangeable and water-soluble phase of soil that are bioavailable to the grape skin (Pinto et al., 2015), which was also the case with deionised H_2O as the extractant.

Topsoil versus grape pulp. For extracting Ba and Sr bioavailable fractions from the topsoil, which correlated with the concentrations in the pulp (R=0.43−0.90 and R=0.40−0.65, respectively, $p<0.01$; Table 8.3.4, Appendix 3), all the tested extraction procedures were appropriate. In addition, the V concentration in the pulp was correlated with its concentration extracted from the topsoil by Na_2EDTA (Figure 5.2.4e).

Topsoil versus grape seed. According to the obtained results in this experiment, the extracted Cr, Cu and Ni concentrations in the seed correlated with the Cr, Cu and Ni

concentrations deionised H_2O 2 h soil extract (Figure 5.2.4a,b,d; Table 8.3.4, Appendix 3). According to the literature, Ni from soil is mobile at pH 4.5–6.5, and it could be bioavailable to leaves and seeds (Kabata–Pendias and Mukherjee, 2007).

Finally, the most bioavailable element using the applied single extractions was Ba. All extracted mobile fractions of Ba from soil were correlated with its concentrations in all investigated grapevine parts (seed, pulp, skin and leaves). In the vineyard soil Ba could originate from frequent application of agrochemicals such as pesticides (rodenticides) and P-fertilisers (Ba-enriched carbonate and phosphate minerals in agricultural fertilisers), as well as aerial sources such as industrial or traffic activities (in diesel engines Ba could be present as additive) (Kabata–Pendias and Mukherjee, 2007; Kravchenko et al., 2014). When Ba once emits into the air, it deposited on the Earth's surface where it further could accumulate in both soil and grapevine parts. The significant correlation for Cr was only observed between the concentration in the seed and the topsoil extracts using H_2O. This result suggests that only soluble Cr can be uptaken by the grapevine and translocated to the seeds in some specific way. A mechanism of the Cr organic compound complex uptake and transportation through the plant xylem could influence its bioavailability and could imply that such complexes could reach the plant parts (Juneja and Prakash, 2005) such as the seed. According to PCA and correlations between the Cu concentration in topsoil extract isolated with Na_2EDTA and its quantity in the leaf and the skin could imply that the main source of Cu in the air-exposed grapevine parts could be the fungicides foliar application. Agrochemical grapevine treatments with pesticides which contain some quantities Cr and Cu (Thomas et al., 2012) in the beginning of the grapevine seasons (before the seed set phase) could probably lead to their accumulation in the seed, which could explain these positive correlations between the concentrations of Cr and Cu (extracts with deionised H_2O) and measured in the seed (Table 8.3.4, Appendix 3). Although, the pseudo-total concentrations of Cd in the topsoil were above MAC (Figure 5.2.1) this element was not easily soluble and bioavailable to the grapevine leaves and berries. The obtained mobile quantities of Cd in the soil were low and cannot affect the grapevine, (Table 8.3.1, Appendix 3) in the weakly acidic to neutral soil in the commercial vineyard. Moreover, the grapevine (*Vitis vinifera*) probably might not be a typical accumulator species (Hall, 2002; Alagić et al., 2015), which is important

because Cd is one of the most eco-toxic elements in the environment. According to the significant associations between Mn concentrations in the topsoil and grapevine parts, the Mn mobile fractions extracted by unbuffered neutral salt solutions could originate from the air deposition on the soil surface caused by the application of Mn-pesticide. In addition, the quantity of Mn in all studied grapevine parts was mutually correlated (Rz/xy) (Figure 5.2.2). Thus, as previously noted, the application of Mn-pesticides predominantly influenced the concentration of Mn in grapevine parts, which were directly exposed to the air (leaf and skin, higher correlation coefficient Rz/xy) than to the inner parts (pulp and seeds).

5.2.1.4 Assessment of PTE bioavailability from subsoil (30−60 cm; B horison) to grapevine parts (seed, pulp, skin and leaf)

Only for concentrations of Al, As, Ba, Cd, Cr, Cu, Li, Ni, Pb, Sb, Sr and V, the significant ($p<0.05$) differences between the topsoil and the subsoil were observed. In this subsection, in parallel PCA and correlation analysis were only applied to the PTE concentrations which statistically differ from the topsoil.

Subsoil versus grapevine leaf. According to the PCA and correlations, the most suitable for extracting from the subsoil Ni and V, which were in correlation with Ni and V concentrations in the leaves was weak salt solution of $CaCl_2$; for Ni, it was also suitable NH_4NO_3, and for Sr, the deionised H_2O 16 h was suitable (Figure 5.2.5a,b,c; Table 8.3.4, Appendix 3).

Subsoil versus grape skin. Unbuffered salt solutions $CaCl_2$ and NH_4NO_3 were the most appropriate for assessing the bioavailability of Ni and Sr from the subsoil and the skin (Figure 5.2.5a,b) as it was also observed for the topsoil. For extracting bioavailable Al, the most suitable was Na_2EDTA (Table 8.3.4, Appendix 3).

Subsoil versus grape pulp. The Sr concentrations from the grape pulp were correlated with Sr concentrations extracted with all tested extraction procedures (Table 8.3.4, Appendix 3). Deionised H_2O 16 h was the most suitable for extracting concentrations of Al, Cu and V that were correlated with their concentrations in the pulp (Figure 5.2.5c; Table 8.3.4, Appendix 3). Na_2EDTA was suitable for isolating V concentration from the subsoil, which was correlated with its concentration measured in the pulp (Figure 5.2.5c; Table 8.3.4, Appendix 3).

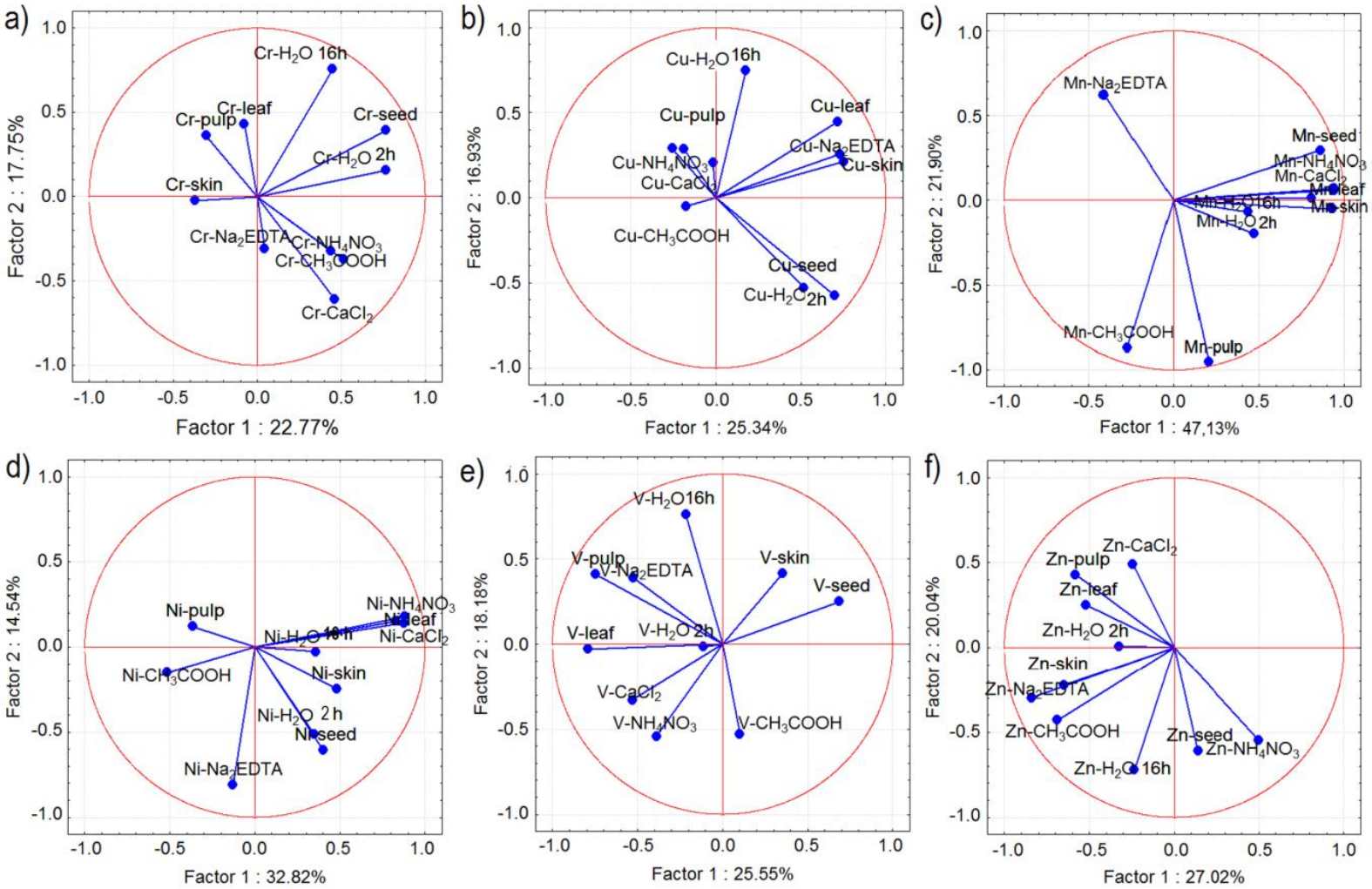


Figure 5.2.4 PCA of the elements in topsoil extracts and grapevine parts (leaves, skin, pulp and seed): a) Cr; b) Cu; c) Mn; d) Ni; e) V; f) Zn (Milićević et al., 2018a).

Subsoil versus grape seed. The concentrations of Ni and Sr extracted from the subsoil using $CaCl_2$, were significantly correlated (Figure 5.2.5a,b; Table 8.3.4, Appendix 3) with the concentrations of Ni and Sr from the seed. For the Ni extracted from the subsoil which correlated with Ni from the seed, beside $CaCl_2$, appropriate were also NH_4NO_3 and deionised H_2O during 2 h and 16 h (Figure 5.2.5a; Table 8.3.4, Appendix 3).

As it was the case with the investigated topsoil in this experiment, Ba was the PTE which showed significant correlations (R=0.51−0.96, $p<0.01$; Table 8.3.4, Appendix 3) between the concentrations extracted from the subsoil and all grapevine parts. All the tested single extraction procedures in this experiment were suitable for the extraction of Ba which was potentially bioavailable to the all investigated grapevine parts (Table 8.3.4, Appendix 3) same as it was observed for Ba from the topsoil. These results imply that Ba, which is not an essential element for the grapevine growth (Oliveira et al., 2010), was the most bioavailable PTE for the grapevine among all the determined PTEs, and the vineyard soil represents the major Ba source in the investigated vineyard ambient. In addition, Sr is also non essential for plant growth (Oliveira et al., 2010), and because of its similar geogenic and biochemical characteristics with Ca (similar ionic radius), it has the ability to compete with Ca and to trap its place in plant (Kabata–Pendias and Mukherjee, 2007).

Among the six single extraction procedures applied in this experiment for extracting easily available or bioavailable PTE fractions from the soil, and according to PCA and correlation analyses it could be concluded that $CaCl_2$, NH_4NO_3 and Na_2EDTA (Table 8.3.4, Appendix 3) were assessed as the most suitable extractants for predicting the elements' bioavailability from both the topsoil and the subsoil to the grapevine leaves, skin, pulp and seed. In addition, deionised H_2O was appropriate for extracting some of the measured PTEs (Ba, Cr, Cu, Sr, Fe, Ni and V) that are potentially bioavailable for the grapevine leaves, grape seed and skin. This results confirm that single extraction procedure using deionised H_2O, which was previously recommended in Experiment 1 as an alternative and cost-effective procedure (Milićević et al., 2017a), was suitable for assessing the bioavailable fraction of some PTEs from the soil.

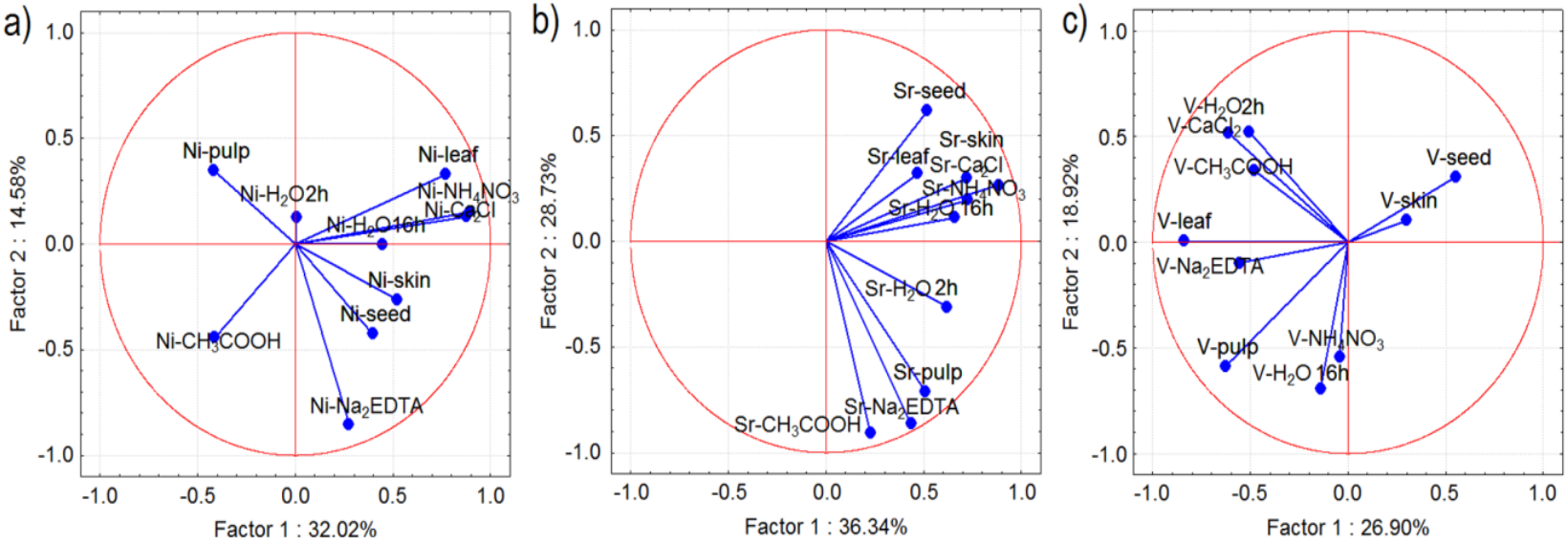


Figure 5.2.5 PCA of the PTEs in subsoil extracts and grapevine parts (leaves, skin, pulp and seed): a) Ni; b) Sr; c) V (Milićević et al., 2018a).

5.2.2 Environmental implications assessment

5.2.2.1 Contamination factor

To investigate whether there are any environmental implications caused by the PTE concentrations in the topsoil and the subsoil soil, CFs were calculated. The obtained CF values for Al, As, Be, Cu, Fe, Mn, Ni and Zn indicated that some of the topsoil samples in the vineyard were moderately contaminated (1≤CF≤3; Likuku et al., 2013) (Figure 5.2.6a; Table 8.3.5, Appendix 3). For B, Cd, Co, Cr and Ni, calculated CFs for all topsoil samples were higher than 1 which indicate moderate pollution of the topsoil. All the elements with CF>1 (Figure 5.2.6a; Table 8.3.5, Appendix 3) imply that there could be some accumulation of the PTEs in the soil from the vineyard parcels because the PTE concentrations in the cultivated parcels were higher than PTE concentrations in the local background soil. However, the CF calculated for Cd (CF≥6) indicated very high topsoil contamination (Likuku et al., 2013) in the vineyard (Figure 5.2.6a; Table 8.3.5, Appendix 3). According to the findings from previous section, based on PCA and correlations (sections 5.3.1.3 and 5.3.1.4), some of the PTEs, with moderate CF values (Be, Cr, Cu, Fe, Mn, Ni and Zn), could be bioavailable to the grapevine parts e.g., Be, Cu, Mn and Ni to the leaf; Fe, Mn and Zn to the skin; and Cr, Cu and Ni to the seed. Although, the CFs for Ba did not imply contamination, and according to the bioavailability assessment from the previous section, Ba showed a strong ability to be bioavailable to all grapevine parts, which imply that further Ba application in the vineyard could increase the pollution of grapevines with it.

The subsoil samples were moderately contaminated (Likuku et al., 2013) by As, Co, Cr, Mn, Na, Pb, Sb and V (1≤CF≤3; Figure 5.2.6b; Table 8.3.5, Appendix 3). Comparing the CF values for the topsoil and the subsoil, it could be seen that CFs for Cd, B, Co and Cu in the topsoil were higher than in the subsoil (Figure 5.2.6a,b). However, CFs for As, Pb and Sb in the subsoil were higher than those CFs obtained for these PTEs in the topsoil (Figure 5.2.6a,b).

Comparing the CF values obtained for the topsoil and the subsoil samples, it could be assumed that in the topsoil predominant quantities of Cd, B, Co and Cu probably origin from the anthropogenic sources (agricultural activities). Overall, CFs for Cd, Co and B also imply the topsoil pollution, and according to previously applied PCA and correlations, they were not bioavailable to the grapevine parts. Nearby or

remote anthropogenic pollution sources (nearby located metal foundry or highway road, Figure 3.3) could emit the PTEs into the air, and the emitted elements could be transported and precipitated into the surface of the soil (O horison, Figure 2.5). The CFs obtained for Zn were comparable with those obtained for topsoil from the experimental vineyard presented in Experiment 1 (Milićević et al., 2017a).

Those elements with the CFs higher in the subsoil than in the topsoil (As, Pb, Sb and V) and those with CFs higher than 1 (Cr and Ni) in the subsoil samples (Figure 5.2.6b), predominantly originate from the geogenic sources, mostly characterising the natural mineralogical composition in the subsoil. As previously mentioned, in the central Balkan Peninsula the geological formations and ore deposits are enriched by As, Cr and Ni concentrations (Dangić and Dangić, 2007; Salminen et al., 2005).

5.2.2.2 Biological absorption coefficient

According to the nonparametric ANOVA test, the concentrations of the grapevine parts (leaf, skin, pulp and seed) were significantly different ($p<0.05$). The bioavailability of PTEs to a plant (and its parts) is a complex process depending on the PTE concentrations in the surrounding media (e.g., soil and air), the soil physicochemical characteristics and the plant affinity for PTEs bioaccumulation (Hall, 2002). The grapevine leaf and grape parts (skin, pulp and seed) have different accumulation abilities for the elements (Hall, 2002; Alagić et al., 2015). According to calculated BAC for assessment of the PTEs bioaccumulation in the grape seed, pulp, skin and leaves, the BAC values for most of measured PTEs were lower than 1. The exceptions were Ca with BAC value higher than 1 (BAC>1) for seed and leaf, and K for all grape parts except the leaf (Table 8.3.6, Appendix 3). The grapevine parts of the investigated varieties in this experiment, which are typical for worldwide wine production, were not hyper-accumulator plants of PTEs and carcinogenic elements which originate from the soil. Anyhow, the calculated BACs were compared for better understanding the elements bioaccumulation ability in the different parts of the investigated grapevine.

Observing the BAC values, the grape seed can accumulate Cu from the topsoil and the subsoil (the highest BAC values), while the leaf accumulated Zn from both soil layers (Figure 5.2.7a,b; Table 8.3.6, Appendix 3).

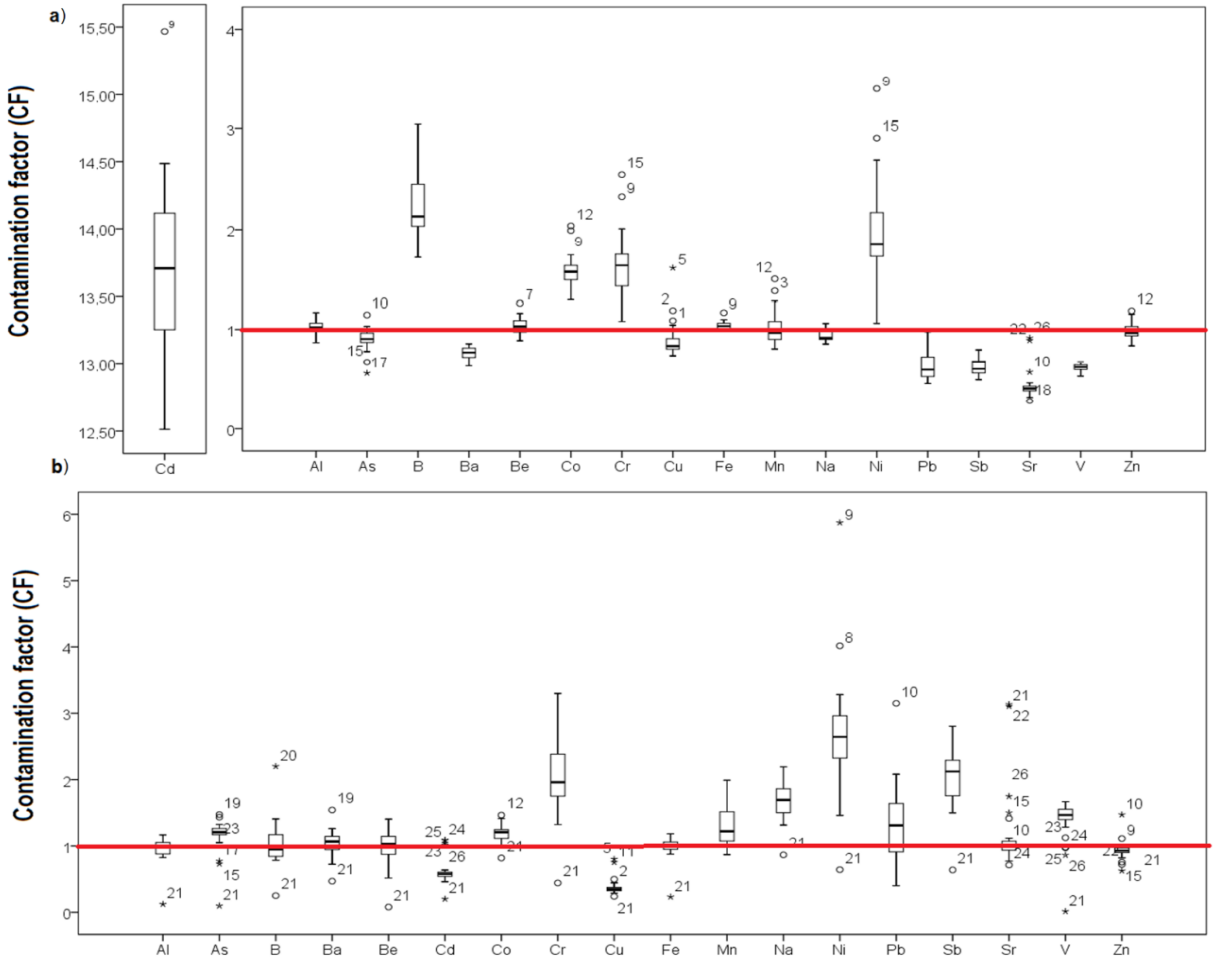


Figure 5.2.6 CF values (-) of potentially toxic elements (PTEs) calculated for the a) topsoil samples b) subsoil samples; the middle line of the box represents the median value of CF, top and bottom represent first and third quartiles and whiskers represent maximum and minimum CF values; "○" represent outliers and "*" represent extremes (Milićević et al., 2018a).

In this experiment, the BAC obtained for Zn (BAC=0.19) was multiple times lower than in Experiment 1 conducted in the experimental vineyard (Milićević et al., 2017a), where *Cabernet sauvignon* leaf was considered as a good bioaccumulator of Zn from the topsoil (BAC=1.36). It is important to note that in the analysed soil in Experiment 1, pH values were lower than in the soil from this experiment. Accordingly, it seems that pH value has a high influence on Zn uptake and accumulation and greatly affects the ability of *Cabernet sauvignon* leaves to be Zn accumulators from the soil as reported by Bravo et al. (2017).

For other investigated PTEs (Al, As, Cd, Co, Cr, Fe, Ni, Pb, Sb and V), the grapevine leaves had the higher BACs than the seed, while for the grape skin and pulp the lowest BAC values were obtained (Table 8.3.6, Appendix 3).

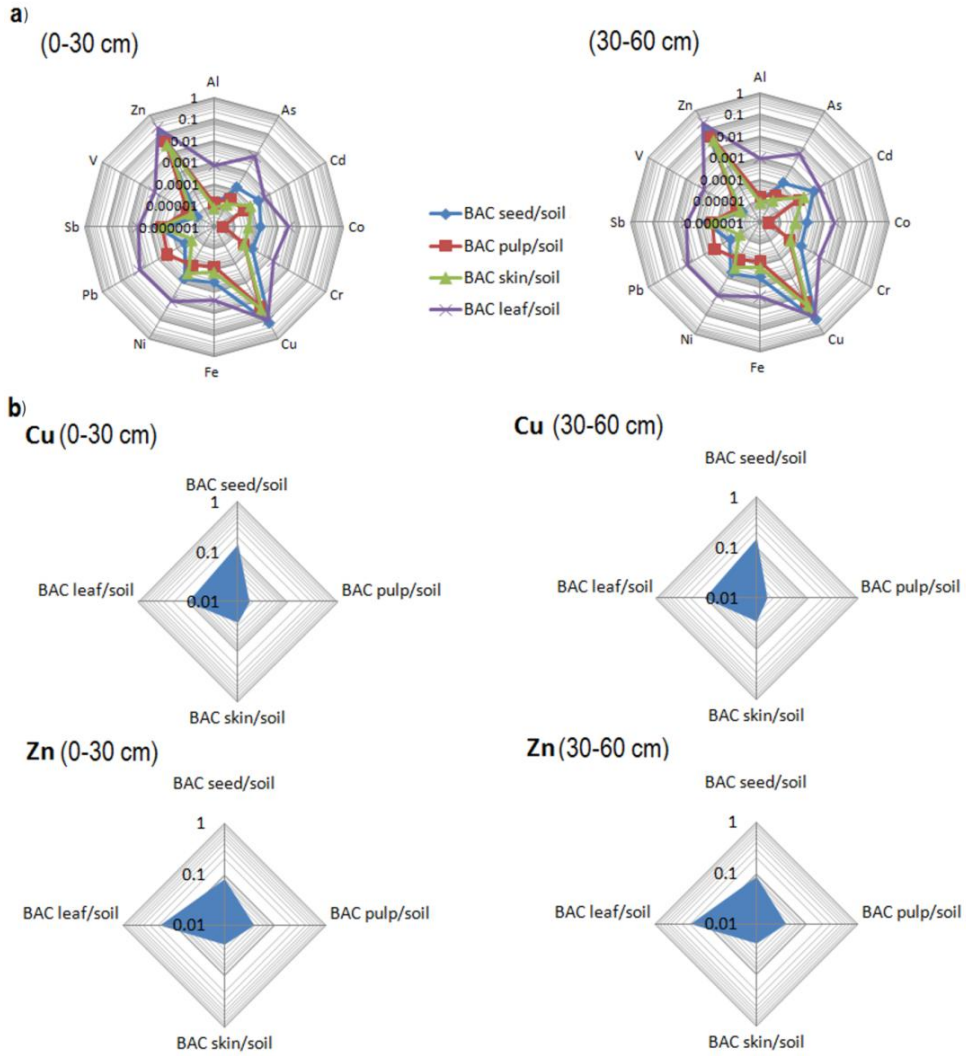


Figure 5.2.7 a) BAC (-) describing the bioaccumulation of PTEs in the grapevine parts; and b) the BAC (-) for Cu and Zn accumulated in the leaf, skin, pulp and seed from the topsoil and subsoil layers (Milićević et al., 2018a).

5.2.2.3 Ratio factor

For most of the investigated PTEs in this experiment (Al, As, B, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, V and Zn) in the grapevine leaves and skin, RF values were above 1 (Table 8.3.7, Appendix 3). Those PTEs in the air-exposed grapevine parts (leaves and skin) could originate also from the air deposition (the foliar application of agrochemicals or anthropogenic activities near the investigated parcels), not only from the soil. Higher RFs obtained for the PTEs were observed in the leaf than in the grape skin (Figure 5.2.8; Table 8.3.7, Appendix 3), probably due to the leaf rough and larger surface that could entrap more airborne particles than the berry's smooth and spherical surface (skin). The $RF_{leaf/seed}$ values for Ba were lower than 1, while the $RF_{leaf/seed}$ value for Mn was above 1. Again, lower $RF_{leaf/seed}$ for Ba confirms the previous allegations that the soil is the main source of this element and it is bioavailable to the studied grapevine parts, while the $RF_{leaf/seed}$ value above 1 for Mn imply the previous allegations that the foliar application of Mn-pesticides could be the main source of this element in the commercial vineyard ambient. Finally, soil from vineyards could represent a diffuse source of pollution (WHO, 2006; Viana et al., 2008) by As, Cr, Cu, Ni, Fe and V, which can be resuspended into the air and deposited on the grapevine leaves and grapes as it will be further discussed in Experiment 4 (Milićević et al., 2017b).

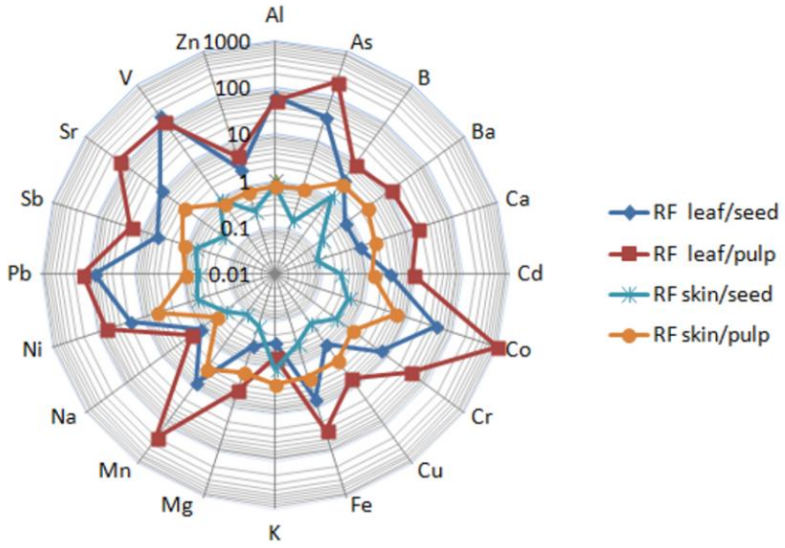


Figure 5.2.8 RF (-) for the PTEs describing the contamination originating from the air deposition (Milićević et al., 2018a).

5.2.3 Non-carcinogenic and carcinogenic health risk assessment for field workers and grape and wine consumers

To simulate exposure processes similar to the real ambient conditions, as much as possible, it is important to set a site-specific exposure scenario for the investigated ambient, including site-specific environmental and exposure parameters, which matched the local lifestyle. For indicating the health risk assessment, the worst-case scenario was observed. Among the measured elements, those that have toxicological reference values such as Reference Dose (RfD), Reference Concentration (RfC), Cancer Slope Factor (CSF) and Inhalation Unit Risk (IUR) were used for health risk assessments (Table 3.4).

For the field workers, who were chronically exposed to the soil in the commercial vineyard during entire grapevine season (from April to October), the health risk assessment indicated that there was a non-carcinogenic risk (HI<1) observed for the field workers (Figure 5.5.9a; Table 8.3.8, Appendix 3). The oral intake had the highest impact on HI which leads to further ingestion and risk for workers health (Figure 5.2.9a). The total carcinogenic effect was in the range from 10^{-4} to10^{-6} (Figure 5.2.9b; Table 8.3.8, Appendix 3), which was within the acceptable range proposed by EPA (US EPA, 2005).

The health risk assessed for the consumers of the grapes and wine indicated that the non-carcinogenic risk for the human intake of grape (adults and children) and wine (adults) were lower than 1 (HI<1) (Figure 5.2.10a; Table 8.3.9, Appendix 3) even in the case of the assessed worst-case scenario. Thus, the PTE concentrations obtained in the grapes and wine did not have adverse impact on human health. The total carcinogenic risk obtained for the grape (adults and children) and wine (adults) consumers were low, $R \leq 1.7 \times 10^{-5}$ and $R \leq 10^{-6}$, respectively (Figure 5.2.10b; Table 8.3.9, Appendix 3). The probability of carcinogenic illness was low for adults and children who regularly consumed the grapes and adults who consume wines (Figure 5.2.10b). Thus, both the studied grapevine varieties in this experiment (*Cabernet sauvignon* and *Sauvignon blanc*) and the white and red wine produced in the commercial vineyard are safe for consumption.

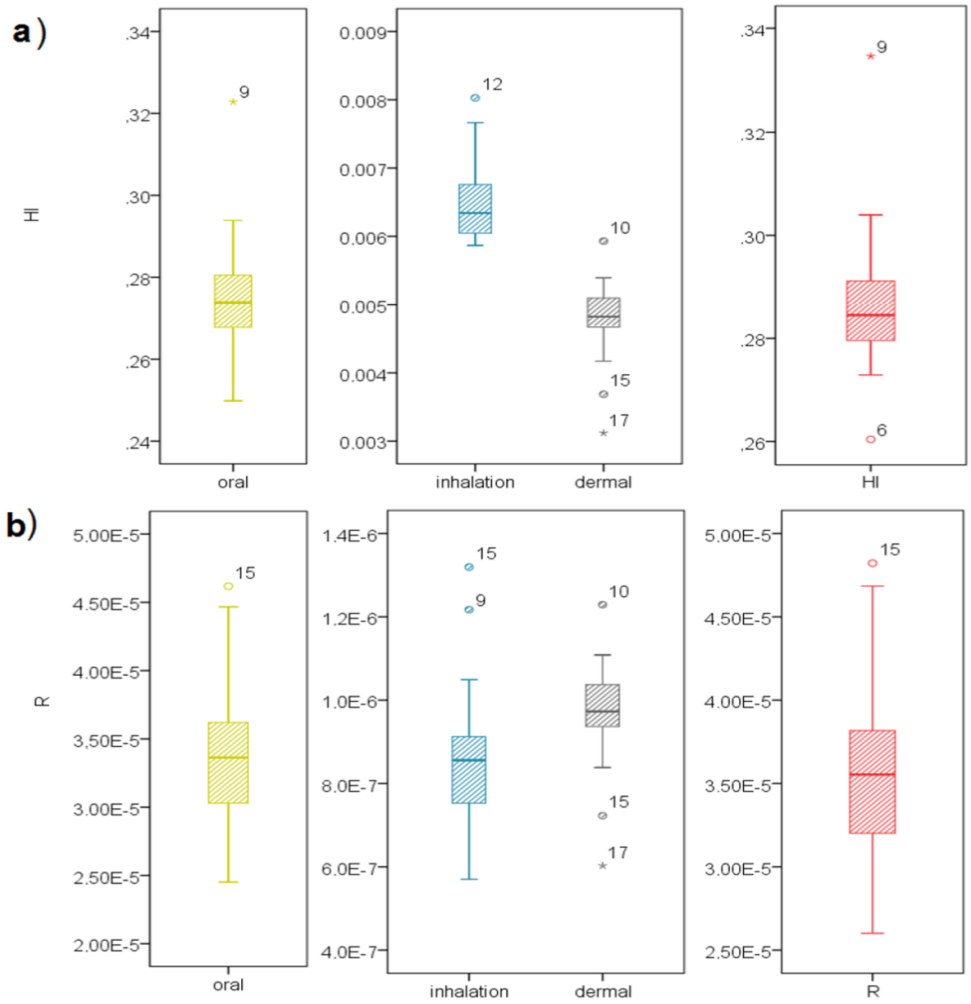


Figure 5.2.9 a) HI (-), and b) R (-) assessment for field workers in the commercial vineyard; (Milićević et al., 2018a).

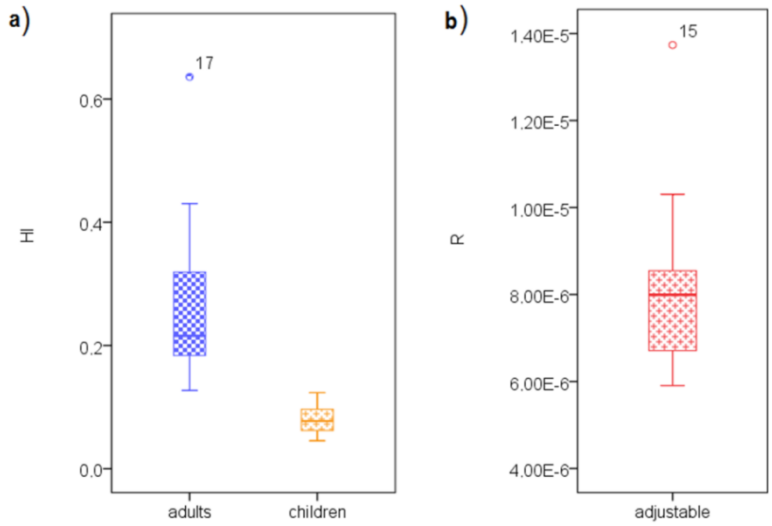


Figure 5.2.10 a) HI (-) for adults and children, and b) adjustable R (-) assessment for the grape and wine consumers (Milićević et al., 2018a).

The results from the Experiment 2 were published in the international journal *Science of the Total Environment* (Manuscript: *Bioavailability of potentially toxic elements in soil–grapevine (leaf, skin, pulp and seed) system and environmental and health risk assessment*; Milićević et al., 2018a). After this comprehensive experiment conducted in the harvest period in the commercial vineyard, our further interest was focused on the seasonal variation of the PTEs in the soil and the grapevine leaves collected on a monthly base through the entire grapevine season also in the commercial vineyard. Moreover, the experiment was performed in order to obtained are there any temporal trends of environmental implications, and mobility and bioavailability of PTEs were assessed through the grapevine growing phases (from the pre-grapevine treating period to the harvest period).

5.3 Experiment 3: Environmental implications and bioavailability risk in the commercial vineyard through entire grapevine season (from pre-agrochemical treatment to harvest period)

5.3.1 Environmental implications of PTEs − temporal patterns of the soil pollution assessment

5.3.1.1 PTEs in the soil samples through the entire grapevine season

Studied soil samples collected through the entire grapevine season were neutral (pH≈7) with low content of OM and high values of CEC (Table 8.4.1, Appendix 4), which is comparable with the physico-chemical parameters obtained for the studied soil collected in harvest period described in Experiment 2 (Milićević et al., 2018a) and the report for the same vineyard area, presented by Ninkov et al. (2014).

Descriptive statistics of 23 element (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sr, V and Zn) concentrations obtained in the soil samples through the all grapevine season using six single extraction and pseudo-total digestion procedures (Table 3.1) are presented in Tables 7.4.2, 7.4.3, 7.4.4, 7.4.5, 7.4.6, 7.4.7 and 7.4.8, Appendix 4. According to the Kolmogorov-Smirnov test, the element concentrations in the soil did not have the normal distribution through the investigated grapevine growing season. Applying the Wilcoxon Signed Rank Test, the significant ($p<0.05$) differences were observed between B, Ba, Cd, P, Pb, S, Sr, V and Zn concentrations in the topsoil through the season, while in the subsoil the differences between B, Cd, Co, Cr, Cu, Mn, Pb, S, Sb, Sr, V and Zn concentrations were observed through the season. The concentration of Cd was increasing in the topsoil samples through the season (Table 8.4.2, Appendix 4), as well as in the harvest period (Experiment 2). The concentration of V was decreasing during the season in the topsoil and increasing in the subsoil (Table 8.4.2, Appendix 4), which imply its leaching from the topsoil to the subsoil (Wierzbowska et al., 2016). In the phase of grapevine leaf development (May), the concentration of Zn in the soil was higher than in other phases and its concentration in the topsoil was continuously decreasing through the grapevine season (Table 8.4.2, Appendix 4).

According to the applied Wilcoxon Signed Rank Test, the significant ($p<0.05$) differences were observed between the concentration of PTEs in the topsoil and subsoil

for some of the determined elements. The concentrations of As, Ba, Be, Cr, Ni, Pb, Sr and V were higher in the subsoil layer than in the topsoil (Table 8.4.2, Appendix 4), which point to their geogenic origin. As previously explained in Experiment 2, in the Balkan Peninsula, As (Dangić and Dangić, 2007), Cr, Ni and Pb (Jakovljević et al., 1997; Antić-Mladenović et al., 2016; Ličina et al., 2017; Dangić and Dangić, 2007; Salminen at al., 2005) could be constituents of the ore deposits and the geological formations. Although, B, Cd and Co concentrations were significantly higher in the topsoil samples than their concentrations obtained in the subsoil samples (Table 8.4.2, Appendix 4). Still, B and Cd probably originated from the agrochemical applications in the vineyard ambient, while Co probably originated from the frequent traffic activities near the vineyard parcels (usually Co originates from fuels synthesis and chemical catalysis) or the agricultural machines' movements (Kabata–Pendias and Mukherjee, 2007) through the investigated parcels during the agrochemical treatments. As observed in the harvest period described in Experiment 2, the concentrations of Cr, Ni and Cd (Table 8.4.2, Appendix 4) in the topsoil and subsoil in other investigated periods (from April to August) were also above MAC (Official Gazette, Republic of Serbia 88/2010; EU Council Directive 86/278/EEC).

Observing the calculated median MF% for the entire grapevine season, the single extraction procedures using deionised H_2O (during 2 h and 16 h) were the least effective for the element extraction from the vineyard soil (Table 8.4.9, Appendix 4). In these deionised H_2O extracts the ionic strength was low, but prolongation of the extraction time influenced that this non-conventional extraction procedure could be more suitable than other for extracting PTEs from the soil, but also less expensive, as it was observed in the previous Experiments 1 and 2 (Hooda, 2010; Milićević et al., 2017a; Milićević et al., 2018). The unbuffered weak salt solution $CaCl_2$ was not suitable for extracting As, Ca, Pb and Sb, while NH_4NO_3 was not suitable for extracting As, Cd and Sb from the topsoil and subsoil (Table 8.4.5, 8.4.6 and 8.4.9, Appendix 4). Studying the available literature, $CaCl_2$ has a high selectivity for the PTEs extracting from the soil, but the high Ca concentration interferes with determination of PTEs and makes it not the best extractant for isolating all PTEs from the soil. Further, Na_2EDTA, which is the chelating agent, was not suitable for extracting the exchangeable Na and Sb from the soil, but it was appropriate for the other PTEs. Observing calculated MF% (Table 8.4.9,

Appendix 4), Na_2EDTA was the most efficient for extracting most of the measured PTEs (Al, As, Ca, Co, Cu, Fe, Mn, Ni, P, Pb and Sr) (Table 8.4.9, Appendix 4). As previously mentioned (Experiment 2) Na_2EDTA has been proven as the most effective and selective extractant for the PTEs with which it usually builds very stable complexes (Inczédy, 1976). The low acid solution of CH_3COOH was the most suitable for extracting Be, K, Mg, S and Sb (Table 8.4.9, Appendix 4). Moreover, CH_3COOH as more aggressive extractant extracted also Cd, Co, Cr, Fe, Mn, Ni, P, V and Zn in higher concentrations than weak salt solutions and deionised H_2O (Table 8.4.9, Appendix 4). The MF% results obtained from the whole grapevine season in this study were comparable with MF% values obtained for the soil sampled in harvest period presented in Experiment 2 (Milićević et al., 2018a).

5.3.1.2 Assessment of environmental implications and bioavailability risk through the grapevine season in the commercial vineyard ambient

Soil CFs for the PTEs through the entire grapevine season. CFs were obtained to investigate whether there any environmental implications caused by the element concentrations in the topsoil and subsoil in the vineyard parcels comparing with local background soil sample through the investigated grapevine season (Table 8.4.10, Appendix 4). For both soil depths (A and B horisons; Figure 2.5) in the vineyard, the moderate contamination ($1 \leq CF \leq 3$) was observed through the entire season, which could be caused by As, B, Co, Cr, Mn, Ni, Pb, Sb and Sr concentrations in the soil from the investigated vineyard parcels (Figure 5.3.1). As previously mentioned in Experiment 2 some of these elements (As, Cr, Ni and Pb) probably have a geogenic origin, characteristical for the Balkan Peninsula (Ličina et al., 2016; Dangić and Dangić, 2007; Salminen at al., 2005). According to PCA, significant positive associations between Cr, As and Ni concentrations in the soil samples were obtained, which could imply a similar PTEs origin (Figure 8.4.1, Appendix 4). In addition, the concentrations of Cr and Ni in the vineyard soil were several times higher than those measured in the local background soil sample (Table 8.4.2, Appendix 4), as it was observed in the harvest period (Experiment 2). Thus, probably they have a geogenic origin in the investigated soil (Figure 5.3.1) but it cannot be straightforwardly claimed that all the measured quantities of Cr and Ni in the soil have a geogenic origin because of the proximity of the metal foundry, which could emit elevated concentrations of these elements in the surrounding

vineyard environment. Observing CFs, for Cd, there were obtained very high values (CFs>6) for the topsoil samples (Figure 5.3.1), especially for soil in August (Experiment 2). Namely, Cd originating from the application of P-fertilisers could cause its concentration increases in the agricultural soils (Kabata–Pendias and Mukherjee, 2007). Additionally, the industrial emissions if they are in the vicinity of the agricultural area could be a prominent Cd pollution source (Kabata–Pendias and Mukherjee, 2007). However, PCA implies the association between Cd and Co concentrations in the soil samples, which indicated that these elements have the similar absorption pathway and they could originate from the same pollution source in the vineyard soil (Figure 8.4.1, Appendix 4). Significant ($p<0.05$) associations between the concentrations of As, Co, Mn, Fe and S in soils are specific for minerals present in it (Kabata–Pendias and Mukherjee, 2007). Conversely, only the concentration of Co was not correlated with the concentrations of the above-mentioned elements (Figure 8.4.1, Appendix 4), so it can be assumed that Co could originate in the soil from the frequent traffic in the vicinity of the vineyard parcels (Figure 3.3), the agricultural machines' movements or the metal foundry (Figure 3.3). Higher Sb concentration in the vineyard soil than in the local background sample (Figure 5.3.1) could imply the traffic activities influence on the soil. Furthermore, the CFs of B (Figure 5.3.1; Table 8.4.10, Appendix 4) indicate moderate contamination in the topsoil samples during the grapevine season, and in July and August in the subsoil (Figure 5.3.1), which imply that B-containing pesticides had an influence on the topsoil pollution, while through the season there were probably some leaching of these PTEs in the subsoil (Aparecida de Sá and Ernani, 2016) supported by physico-chemical conditions of the soil (Table 8.4.1, Appendix 4). The median CF obtained for Mn is slightly decreasing in the topsoil through the season, while in August CF in the subsoil was slightly higher than CF in the topsoil (Figure 5.3.1; Table 8.4.1, Appendix 4). The application of Mn-based pesticide (Maneb) especially in phases of the grapevine development could cause this Mn concentration decreasing trend in the soil through the grapevine season (*personal communication*, 2015). In addition, median CFs for As, Ba, Cr, Ni, Pb, Sb, Sr and V were obtained in higher values for the subsoil than for the topsoil, which indicated their dominant geogenic origin (Kabata–Pendias and Mukherjee, 2007).

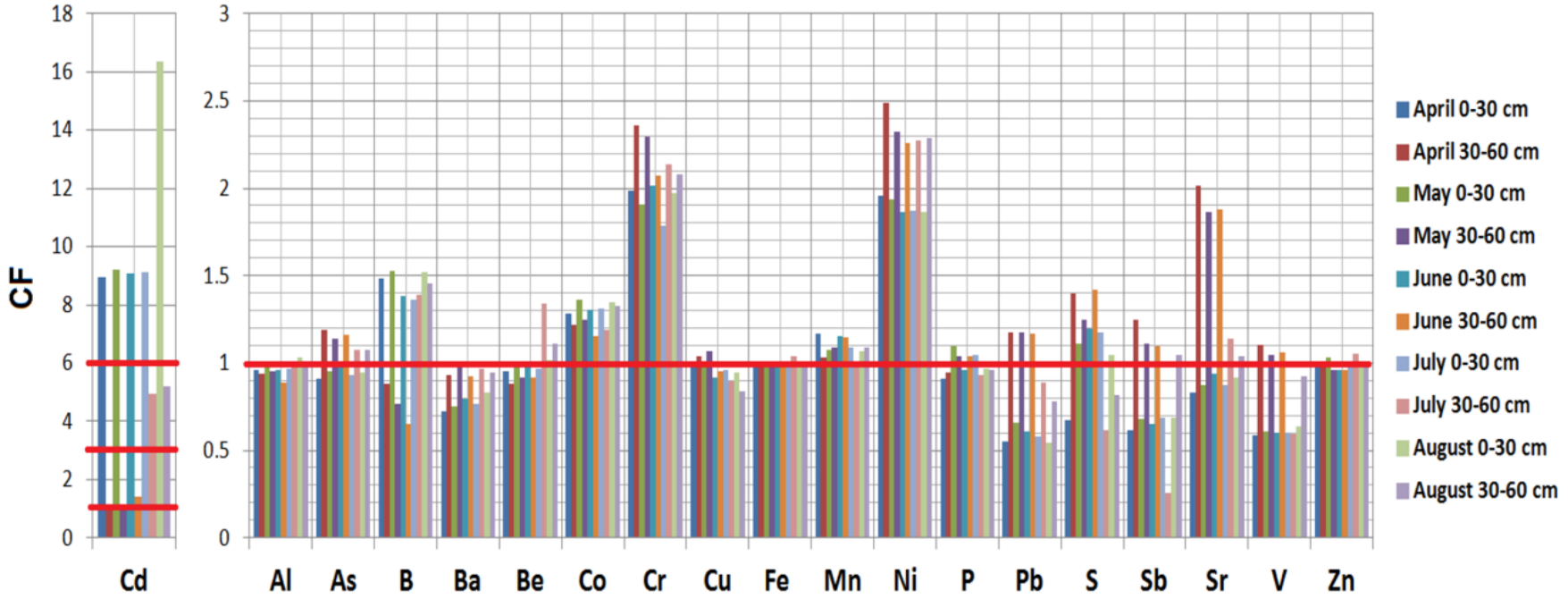


Figure 5.3.1 Element CFs (-) temporal trends through the entire grapevine season and soil depths (Milićević et al., 2018b).

$E_r i$ and RI through the entire grapevine season in the vineyard. Observing the calculated Eri for PTEs, considered by Hakason (1980), low environmental risks of As, Cd, Cr, Cu, Ni, Pb and Zn were observed in the soil samples. In addition, a high environmental risk was observed for Cd in the topsoil collected through the season (Table 8.4.11; Figure 8.4.2, Appendix 4), especially in August when the serious ecological risk was observed (Table 8.4.11, Appendix 4). In addition, in the subsoil, the moderate ecological risk was observed, except in the veraison and harvest periods (July and August) (Table 8.4.11; Figure 8.4.2, Appendix 5) when the risk was high. This high and serious (Guo et al., 2010) environmental risks ($160 \leq Eri < 320$ and $320 \leq Eri$, respectively) obtained for Cd in the topsoil in these periods (Table 8.4.11, Appendix 4) could be a consequence of the frequent grapevine Cd-based agrochemical treatments in the grapevine growing periods and subsequent its leaching and accumulating in deeper soil layers in the end of the grapevine season. Observing the calculated RI in the vineyard ambient, there was a moderate environmental risk ($150 \leq RI < 300$; Guo et al., 2010) through the all grapevine season for the topsoil, except in August when the risk was severe ($300 \leq RI < 600$) (Table 8.4.11, Appendix 4). In addition, in the subsoil, the environmental risk was low through the season ($RI < 100$), only in the veraison and harvest, there were obtained moderate environmental risks obtained for the subsoil (Table 8.4.11; Figure 8.4.2, Appendix 4). Accordingly, some PTE quantities could be leached from the topsoil to the subsoil (Wierzbowska et al., 2016).

BGI values for the topsoil through the grapevine season. Comparing the PTE concentrations in the topsoil with those obtained for the subsoil, the higher BGI values imply higher element sorption in the topsoil (Table 8.4.12, Appendix 4). The median BGI values indicated that there was moderate Cd sorption in the topsoil through the grapevine growing phases with frequent agrochemical treatments (April, May and June, BGIs were 7.81; 8.06; 6.50, respectively) (Table 8.4.12; Figure 8.4.3, Appendix 4). It can also be noticed that during these periods, there were obtained apparent (Mazurek et al., 2017) BGI values for B, and BGIs for Be, Co and Mn (Table 8.5.12; Figure 8.5.3, Appendix 5) were at the limit between low and apparent values. Furthermore, in July, a period with more frequent traffic than in other periods and consequently higher air deposition, there was apparent sorption of Sb in the topsoil (Table 8.4.12, Appendix 4). During the harvest period (August) the BGI values obtained for PTEs were low to

slightly moderate (Table 8.4.12; Figure 8.4.3, Appendix 4), which imply that before the grape harvest there were not agrochemical activities and their influence on the soil decreased. Finally, according to BGIs, there were low Cr and Ni adsorptions in the topsoil (Table 8.4.12, Appendix 4), and as previously described in this experiment and Experiment 2, these elements mostly have a geogenic origin.

BRAI through the grapevine season. By applying a regular equation (using concentrations extracted by Na_2EDTA), $BRAI_{probable}$ and $BRAI_{apparent}$, the medium bioavailability risk was assessed (Table 8.4.11, Appendix 4). Additionally, applying the modified equation (using concentrations extracted by CH_3COOH), $BRAI_{probable}$ indicated medium, but $BRAI_{apparent}$ indicated low bioavailability risk (Table 8.5.13, Appendix 5). However, using regular and modified BRAI equations, significant ($p<0.01$) correlations (R=0.91 and R=0.90, respectively) between $BRAI_{probable}$ and $BRAI_{apparent}$ were observed, that was also proved by the regression analysis between the obtained BRAI values (Figure 5.3.2). The $BRAI_{probable}$ (Na_2EDTA) values were ranged from 1 to 2.67 (Table 8.4.13, Appendix 4) and were slightly lower than $BRAI_{probable}$ obtained for the urban soil in Spain (Madrid et al., 2008), twice or more times lower than $BRAI_{probable}$ values of the mining areas in India (Anju and Banerjee, 2011), the agricultural soils from Italy (Poggio et al., 2009) and residential sites in Italy (Poggio et al., 2009).

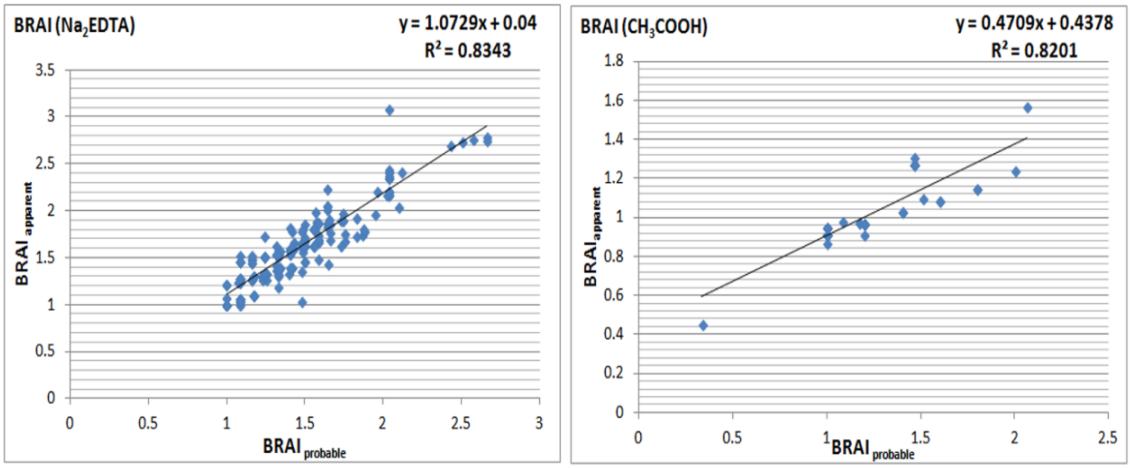


Figure 5.3.2 Relation between $BRAI_{probbable}$ (-) versus $BRAI_{apparent}$ (-), applying a) regular (Na_2EDTA) and b) modify (CH_3COOH) equations; regression equation and coefficient of determination (R^2) are presented above the graph (Milićević et al., 2018b).

5.3.1.3 Associations between the environmental risk, biogeochemical index, and bioavailability risk

In this subsection, only the significant ($p<0.05$) associations between the environmental implication indices will be discussed. According to PCA, there was a significant association between RI and BRAI (Figure 5.3.3a). Comparing the BRAI (Na_2EDTA), BRAI (CH_3COOH) with RI obtained for the topsoil, RI is significantly ($p<0.05$) associated with BRAI (CH_3COOH). Thus, PTEs soluble under the low acid conditions (CH_3COOH) have a higher impact on the bioavailability risk than PTEs complexed with the substrates in the soil. Conversely, the RI was not associated with BRAI values in the subsoil layer (Figure 5.3.3b).

The both regularly calculated $BRAI_{probable}$ and $BRAI_{apparent}$ (Na_2EDTA) only for the topsoil were significantly ($p<0.05$) correlated with the BGI for Cd ($BRA_{probable}$−BGI Cd: R=0.48; $BRAI_{apparent}$−BGI Cd: R=0.40; Figure 5.3.3c). This significant association could imply that moderate Cd sorption (Figure 5.3.3c) could cause both potential and apparent bioavailability risks in the topsoil.

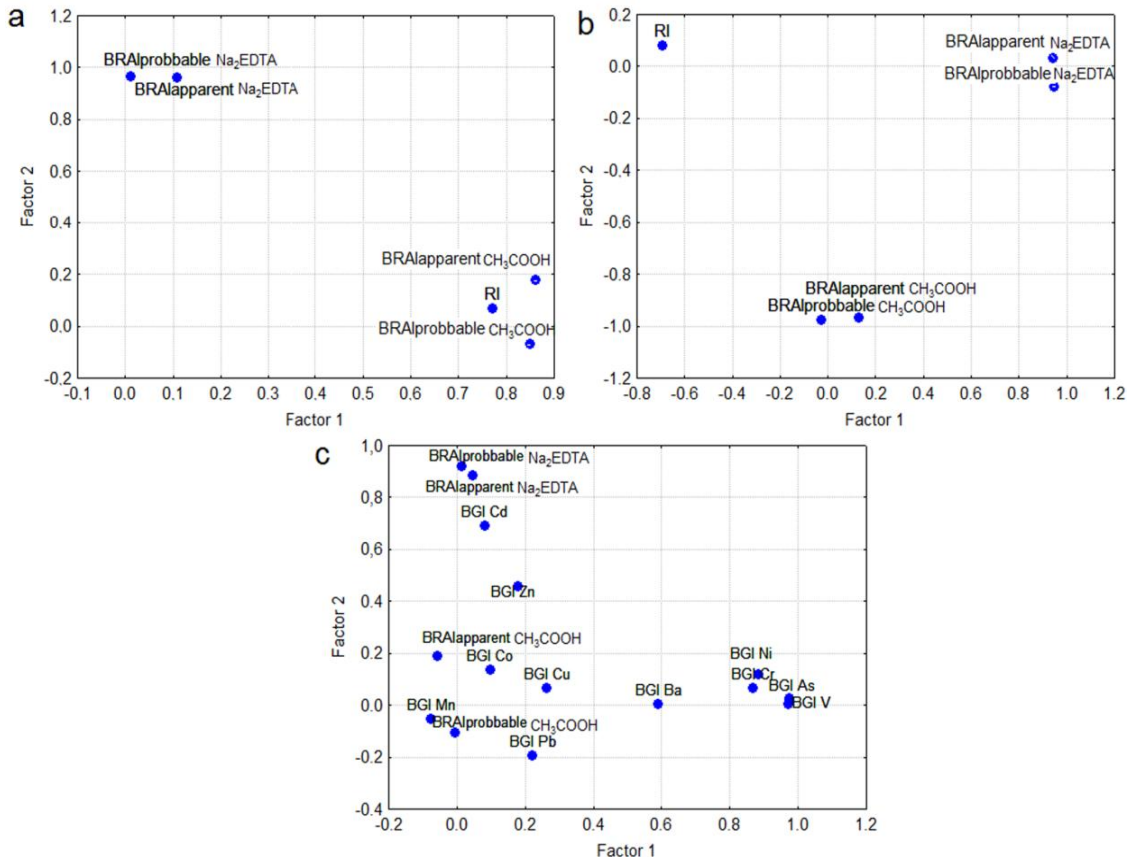


Figure 5.3.3 PCA for a) RI (-) versus BRAI (-) in the topsoil; b) RI (-) versus BRAI (-) in the subsoil; and c) BRAI (-) versus BGI; (-) (Milićević et al., 2018b).

5.3.2 Temporal patterns of the PTE concentrations in the grapevine leaf samples: bioaccumulation and bioavailability

5.3.2.1 The PTE concentrations in the leaf and PTEs bioaccumulation through the entire grapevine season

According to Kolmogorov-Smirnov test, for Be, Cd, Co, Cr, Cu, Fe, Mn, Pb and Sb concentrations in the grapevine leaf, non-normally distributions through the grapevine season (May, June, July, and August) were observed. Medians of Al, B, Be, Cd, Cu, Ni and Zn were decreasing, while medians of Ba, Ca, Co, Mg and Sr concentrations were increasing in the leaf samples collected through the season (Table 8.4.14, Appendix 4).

According to BACs, only the values obtained for Ca and for some samples values calculated for B were above 1 (Table 8.4.15, Appendix 4), which indicate that those two elements can be accumulated from the soil to the grapevine leaves. As in Experiment 2, for the other measured elements, BACs were lower than 1 (Table 8.4.15, Appendix 4) which indicated their low bioaccumulation in the leaves. However, for better understanding different PTEs bioaccumulation abilities to the leaves and for obtaining in which leaf development phase eventually some PTE quantities from the soil could be accumulated in the grapevine leaves, BAC values were observed. According to the PCA (Figure 5.3.4a,b), it could be noticed that there were significant differences in the elements' bioaccumulation in different leaf development phases (May, June, July and August). Increasing the BAC values for Ca through the grapevine season (Figure 5.3.4a,b; Table 8.4.15, Appendix 4) were probably caused by the reinforcement of the grapevine leaves structure (Suárez, 2010). The highest influence of B bioaccumulation to the leaf from the topsoil and the subsoil was observed in June (Figure 5.3.4a,b). During the leaf set (in May), the highest Al, Be, Cd, Cu, Fe, Ni and V bioaccumulations in the leaf were observed in comparison to the other investigated phases. For the leaves sampled in this phase, significant correlations (R=0.78; R=0.48; $p<0.05$, respectively) were observed between Al and Fe and Al and V concentrations. Furthermore, the significant ($p<0.05$) intercorrelations between the BACs of Be, Cd and Ni (Figure 5.3.4a,b) seems to imply the frequent agrochemical applications (Kabata–Pendias and Mukherjee, 2007) in the leaf set phase, which represents the most important phase for leaf development protecting in the vineyard (*personal*

communication, 2015). According to BACs, in June (the leaf development phase), there was the highest bioaccumulation of Cu, K, Na and Zn from soil to leaf (Figure 5.3.4.a,b; Table 8.4.15, Appendix 4). The significant ($p<0.05$) correlations between B, Cu and Zn concentrations (Figure 5.3.4.a,b) indicate that those elements could originate from Cu-based pesticides (Kabata–Pendias and Mukherjee, 2007). Among the investigated grapevine development phases, in July the highest bioaccumulations of As, Co, Cr, Mn, Pb and Sb in the leaf were observed. The significant associations between the BAC pairs: Co−As, Cr−Pb, Cr−Sb, Sb−Pb, Sb−Co, Co−Cr and Cr−Sb (Figure 5.3.4a,b) imply the potential influence of the nearby anthropogenic activities in this phase (Kabata–Pendias and Mukherjee, 2007). This potential anthropogenic influence could be caused by the proximity of the metal foundry or the main road (Figure 3.3) with fluent traffic in July, as it was previously mentioned observing the results for CF. In the harvest phase (August), Ba, Ca, Mg and Sr were the most bioaccumulated in the leaves in comparison to the other investigated phases, and the significant ($p<0.05$) association between their BACs also were observed (Figure 5.3.4a,b). Essential, Mg and Ca are important for conformational stabilisation of macromolecules such as nucleic acids, proteins, cell membranes and walls in leaves (Guo et al., 2016). Not essential for plant growth are Ba and Sr (Oliveira et al., 2010), but because all of them (Ba, Ca, Mg and Mn) are alkaline earth metals with similar geogenic and biochemical characteristics (similar ionic radius), Ba and Sr have the ability to compete with Ca and Mg and to trap their places in plants (Kabata–Pendias and Mukherjee, 2007) as it was previously described for Sr in Experiment 2.

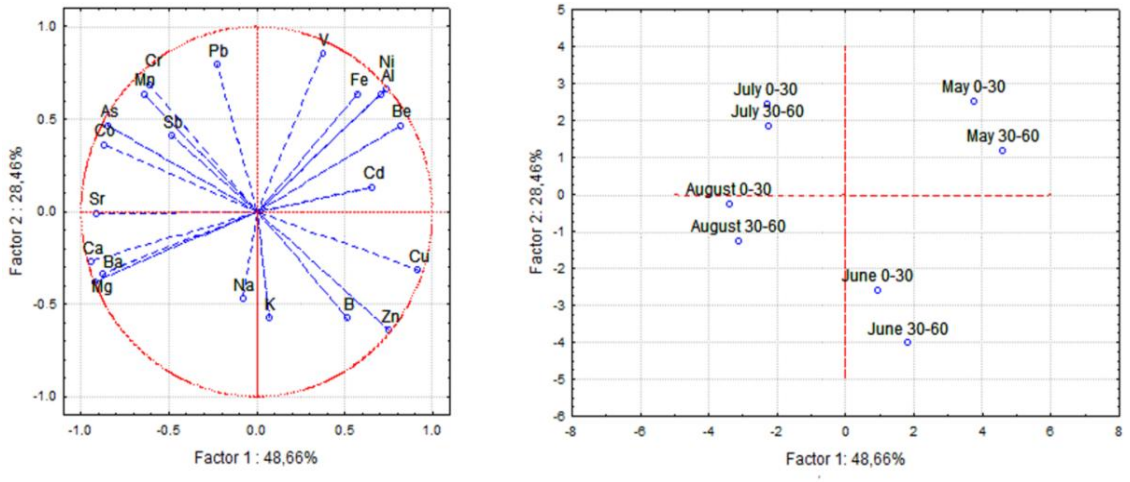


Figure 5.3.4 PCA for the assessment of the associations between the a) BAC and b) the leaf development phases through the season (Milićević et al., 2018b).

5.3.2.2 Correlations between biological accumulation concentrations of the elements in the leaves versus biogeochemical index in the vineyard soil

Higher quantities of Cu and Na in the topsoil samples and higher BGI values were significantly ($p<0.05$) correlated with lower BAC values (Figure 5.3.5). These relations imply the Cu and Na quantities in the topsoil influence to their leaves bioaccumulation. Contrary, for B, Cd, Sb and Sr (Figure 5.3.5a,b,e,f) higher BGI values correlated with higher BAC values imply that other sources contribute to the overall concentration of these PTEs in the leaves. In addition, bioaccumulated B, Cd and Sr in the leaves that are not directly related to the topsoil could originate from the frequent agrochemicals application in the vineyard, while the traffic (Sánchez-Rodas et al., 2017) could influence the Sb accumulation in the leaf.

5.3.3 Assessment of the PTE bioavailability in the soil–leaf system through the entire grapevine season

According to the previously described environmental indices, Cd, Co, Cr, Cu, Mn, Sr and Ni concentrations determined in the soil could have potentially toxic effects on the grapevine leaves or vineyard environment. In addition, if PTEs cause environmental implications, they are not necessarily bioavailable to the leaves (for example as it was observed for Cd in Experiment 2). In order to examine the bioavailability in the soil-grapevine leaf system for these elements, Spearman's correlation between PTEs extracted from the soil using different six single extraction procedures (Table 3.1) with the concentrations in the grapevine leaf were performed.

According to the correlations, there were not obtained any significant correlations between Cd and Co concentrations in the soil extracts and their concentrations measured in the leaves. Namely, as previously explained according to BACs, these two toxic elements could not easily be uptake by the grapevine leaves. Observing determined soil physicochemical parameters (Table 8.4.1, Appendix 4), Cd and Co were probably strongly bounded in the soil (Kabata–Pendias and Mukherjee, 2007). As it was previously explained by the BRAI values, these two elements had a high impact on soil bioavailability risk, but BACs were low, which indicated that the investigated grapevine varieties seem to be Cd and Co excluders.

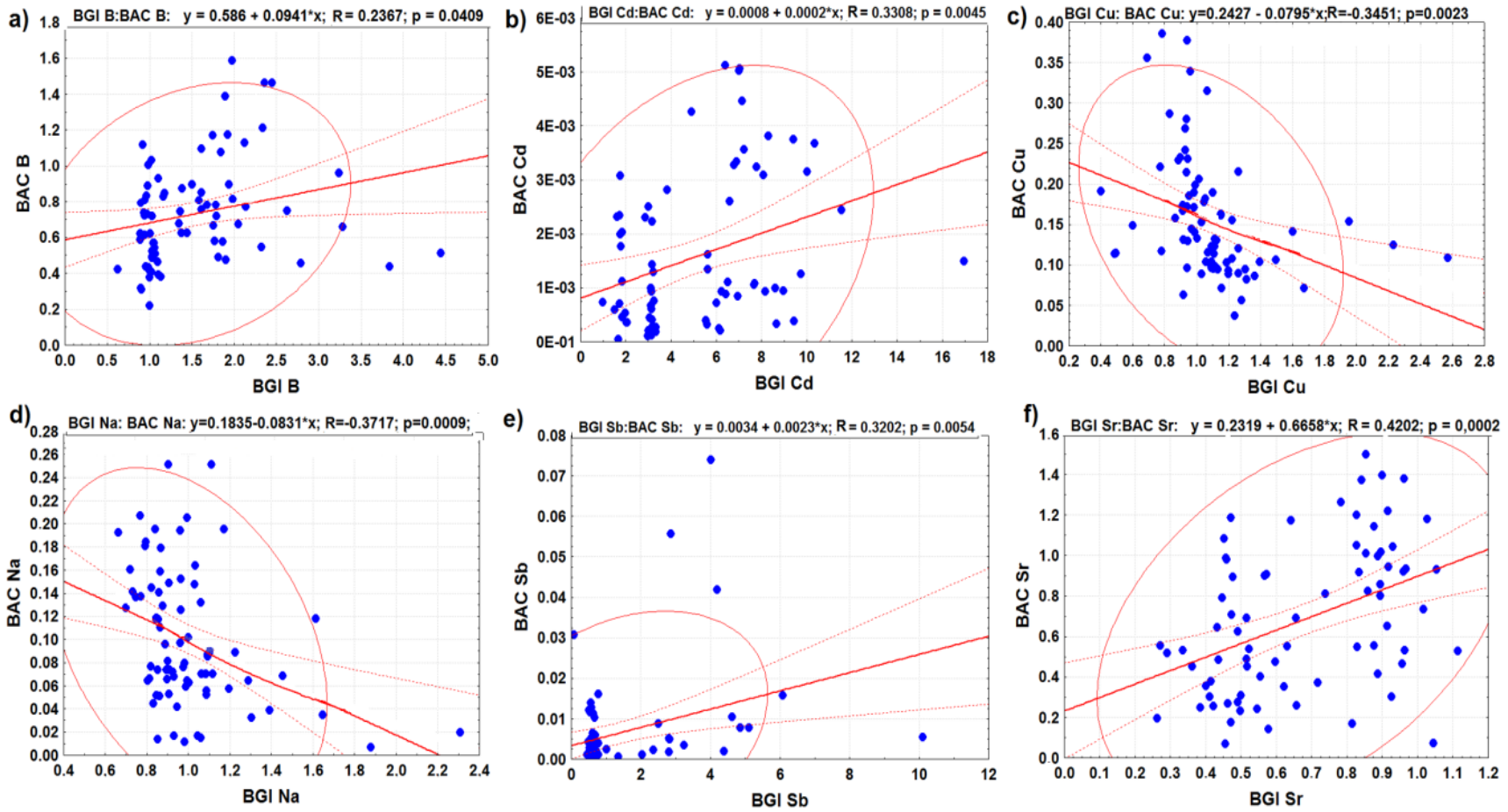


Figure 5.3.5 Correlations between BAC (calculated for topsoil to leaves) and BGI values (-) graphs for a) B; b); Cd; c) Cu; d) Na; e) Sb; and f) Sr; the circles represent the area where the most variables are grouped; the equation of the variable distribution, correlation coefficient (R) and significance (*p*) are presented above the graphs (Milićević et al., 2018b).

The most significant correlation was noticed between the Cr concentration in the leaves and its quantity extracted using Na_2EDTA from subsoil sampled in June (R=0.71; $p<0.05$). Commonly, Cr represents the element with very low mobility abilities, especially under moderate oxidising and reducing conditions, near-neutral pH values and low OM content (Kabata–Pendias and Mukherjee, 2007; Wuana and Okieimen, 2011) which confirmed that the environmental risk obtained for Cr in soil could be directly related to its bioavailability in the soil-grapevine leaf system under the obtained soil physicochemical parameters.

Furthermore, the most significant ($p<0.01$) correlations between the Cu concentration in the leaf and Cu in the extract of topsoil extracted by Na_2EDTA, were observed in June (R=0.83) and in August (R=0.60). As it was previously described, with the correlation between BAC and BGI, Cu adsorption in the topsoil was directly related to the Cu bioaccumulation in the leaves.

The most bioavailable elements in the soil-grapevine leaf system were Mn, Ni, and Sr. According to six single extraction procedures, the most suitable extractants for isolating Mn which is bioavailable from topsoil were the weak salt solutions $CaCl_2$ and NH_4NO_3 and from subsoil $CaCl_2$, NH_4NO_3 and deionised H_2O. The bioavailable Mn were available to the leaf through the entire investigated season (May–August), while the most significant ($p<0.01$) correlations were observed between the PTE concentrations in samples from May and June, which could imply higher Mn uptake by the leaf during its development and growth (R=0.57−0.78). Higher correlation coefficients were observed between the concentrations from the subsoil than from the topsoil. The root system in the vineyard is probably branched and deeper than 0−30 cm (*personal communication*, 2015). Thus, the frequent application of Maneb pesticide through the grapevine season (*personal communication*, 2015) could cause historical accumulation of Mn which leaches in the subsoil. Also, the Mn bioavailability could be directly related to the air deposition on the soil surface, its sorption in the topsoil and leaching in the subsoil that could be directly influenced by the low OM (Vyas et al., 2015), and finally by the bioaccumulation of Mn in the grapevine leaf.

According to the obtained correlations, the concentrations of Ni were bioavailable to the grapevine leaf (R=0.57−0.76; $p<0.01$) under the obtained soil physicochemical conditions (Table 8.4.1, Appendix 4). Moreover, high complexation

ability, low OM and near-neutral pH could influence the high bioavailability of Ni in soils. Generally, the mobility of Ni is inversely related to the soil pH. Nickel can be very easily uptake by the plants and its concentration in the plant is a simple function of the Ni forms in soils. Plants more readily absorbed the ionic Ni^{2+} form than when it is chelated (Kabata–Pendias and Mukherjee, 2007).

Furthermore, bioavailable Sr extracted from the soil using $CaCl_2$ and NH_4NO_3 the most significantly ($p<0.01$) correlated with Sr from the leaf (R=0.55−0.74; $p<0.01$). As previously mentioned, in the soils, Sr is usually present as divalent cation Sr^{2+}, which has competitive ability to trap the places of Ca in the leaves (Kabata–Pendias and Mukherjee, 2007).

After all, the results from this experiment were published in the international journal *Ecotoxicology and Environmental Safety* (Manuscript: *Integrated approach to environmental pollution investigation – Spatial and temporal patterns of potentially toxic elements and magnetic particles in the vineyard through the entire grapevine season*; Milićević et al., 2018b). The air quality monitoring in the presumably low polluted rural ambient have rarely performed and moreover, there are almost not regulatory monitoring stations in agricultural ambients. Therefore, in parallel with Experiments 2 and 3, the air pollution in the commercial vineyard, with frequent agrochemical treatments, was assessed by using active moss bag biomonitoring technique through the entire grapevine growing season. Also, the PTE concentrations in the grapevine leaf were compared to the concentrations measured in transplanted mosses, in order to asses could the grapevine leaves indicate the ambient air pollution in the commercial vineyard. All these results are going to be presented in Experiment 4.

5.4 Experiment 4: Moss bag biomonitoring of air pollution in the commercial vineyard−a contribution to the methodology

5.4.1 Review of the results according to LOQ_T for moss bag technique and exposure periods in the commercial vineyard

The concentrations of 41 PTEs (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, K, Na, Ni, Pb, Rb, Sb, Sn, Sr, Th, Ti, V, Zn, and REEs: Sc, Y, Ga, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in two moss species (*S. girgensohnii* and *H. cupressiforme*) exposed in the vineyard are presented in Table 8.6.1, Appendix 6. Only the concentrations of K, Na, and Rb were below the obtained LOQ_T for the moss bag technique (Table 3.5.1), this implied that concentrations of K, Na and Rb were lower than the initial values in the moss, which were also reported in some previous studies (Adamo et al., 2003; Aničić et al., 2009a, 2009c; Vuković et al., 2017). The concentrations of the other elements, even REEs, were above the LOQ_T in moss from every investigated period. In this experiment, three consecutive periods of 2 months; and one period of 4 and one period of 6 months were simultaneously tested to investigate which period is appropriate for the moss bag biomonitoring of the PTEs in vineyard ambient. In both exposed moss species, for most of the measured PTE concentrations, there were not significant differences ($p<0.05$) in the concentrations among three 2-month bag exposure periods (1M2: March 20th – May 20th; 2M2: May 20th – July 20th; 3M2: July 20th – September 20th). Nevertheless, the median of Al, As, Ba, Ca, Co, Cr, Fe, Sb, Sn, Ti, V and Zn and the REEs concentrations were significantly ($p<0.05$) increasing with prolongation of the moss bags exposure (from 2- to 6-month) (Table 8.5.1, Appendix 5). With exposure time prolongation, the most prominent increases of the PTE concentrations were observed for As, Co, Cr, Cu, Fe and V (Figure 5.4.1). The Cu and Ni concentrations in the 2-month exposure periods were significantly distinguished (Table 8.5.1, Appendix 5). The Cu median concentrations were significantly higher in the 1M2 than the concentrations obtained in 2M2 and 3M2 periods. In addition, the Cu concentrations in the 4-month (M4: March 20th – July 20th) and 6-month (M6: March 20th – 20thSeptembe) exposure periods were higher than those observed in the 1M2 period. The similar trend was observed for the Ni concentrations in the exposed mosses: the highest concentrations were measured in the samples exposed in 1M2 period and they significantly differed from the other studied two month periods

(2M2 and 3M2). Three consecutive 2-month periods during the season gave information about a different enrichment of PTEs in the vineyard ambient (e.g., Cu and Ni), which could indicate the different grapevine agrochemical treatments or other anthropogenic activities nearby. As previously mentioned in Experiment 2, except widely used Cu-fungicide, some P-fertilisers could also contain PTE (Cr, Cd, Cu, Zn, Ni and Pb) concentrations as impurities (Thomas et al., 2012). Finally, the 6-month period (M6) represents cumulative air pollution with PTEs in the vineyard during the entire season.

For active moss bag biomonitoring in different ambients, it is important to establish the specific parameters (e.g., species selection and its exposure). This is the most important for the determination of the moss bag technique applicability in the agricultural areas. According to available literature, only two studies before this experiment were performed in the agricultural areas exposing mosses *Pseudoscleropodium purum* (Capozzi et al., 2016b) and *H. cupressiforme* bags (Capozzi et al., 2016a) and there were not any specific experiment performed in the vineyard area before this one. The results of this experiment performed in the commercial vineyard were comparable with the results obtained in one of those rare experiments in the agricultural area (Capozzi et al., 2016a), which demonstrated that *H. cupressiforme* moss bag could recognise the agricultural area as a significant air pollution source. Comparing two experiments conducted in the agricultural areas of the regional interest, "Campania" in Italy with "Oplenac Wine Route" in Serbia, the moss bags recognised both agricultural areas as diffuse pollution sources including soil PTEs resuspension and agrochemicals influence. The As, Cd, Co, Cu, La, Ni, Mn, Th, Y and Zn concentrations were significantly higher in this experiment than those measured for the Italian agricultural area. Conversely, the Cr, Li, Sb, Sc, Sn and V concentrations were higher in the mosses exposed in the agricultural area in Italy (Figure 5.4.2). In particular, As, Cd, Cu, and Ni concentrations were especially increased in this experiment, which was also observed by the passive moss biomonitoring of PTEs across Europe (Harmens et al., 2010; Barandovski et al., 2012). This phenomenon could be explained, as in previous experiments, with geogenic enrichment of As in soil (Dangić and Dangić, 2007; (Tarvainen et al., 2013) or by the frequent agrochemicals application in the commercial vineyard which can increase Cr, Cu and Ni concentrations in the soils (Thomas et al., 2012).

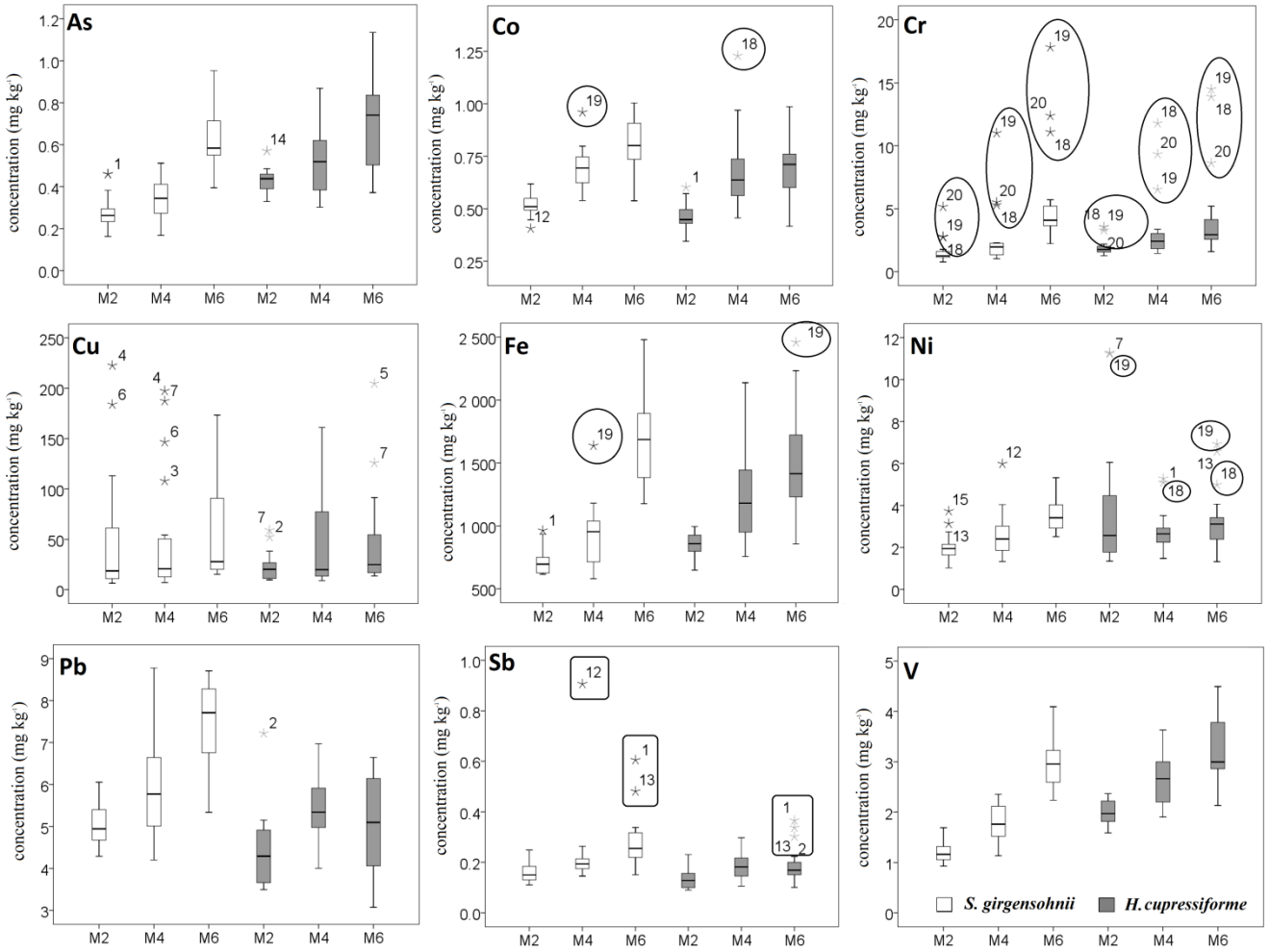


Figure 5.4.1 PTEs accumulation in mosses (*S. girgensohnii* and *H. cupressiforme*.) during three periods exposure M2, M4 and M6 (abscissa represents exposure periods, and the ordinate represents the concentrations − median, standard deviation exposed in mg kg^{-1}) (Milićević et al., 2017b).

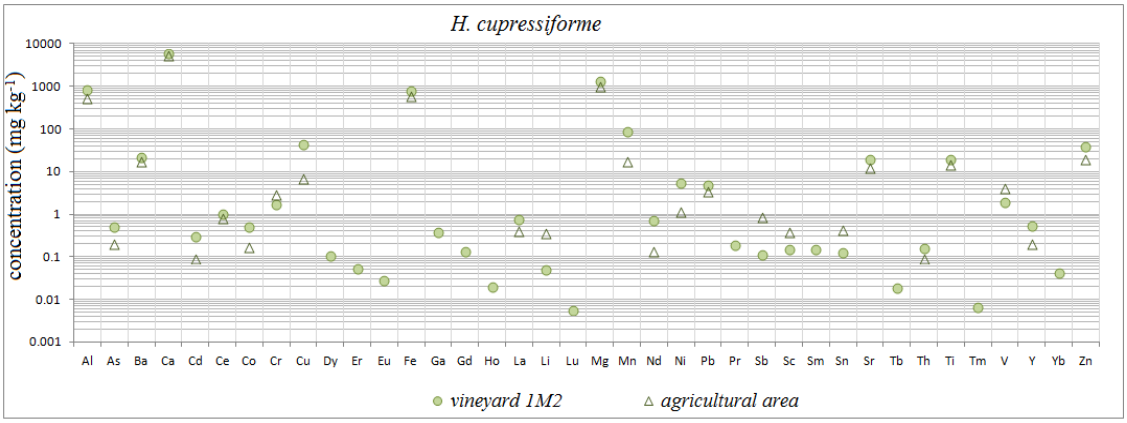


Figure 5.4.2 Median concentration (mg kg^{-1}) of the elements in *H. cupressiforme*: the studied commercial vineyard in Serbia versus the agricultural area in Italy (Capozzi et al., 2016a) (Milićević et al., 2017b).

Many experiments have been performed using various moss species and exposure periods in different urban ambients (Ares et al., 2012). Still, to give an information about the 2-month PTEs enrichment level in two different anthropogenically devastated areas (agricultural and urban), the results from this experiment were compared with the corresponding experiments which were performed in the urban area in Serbia (Belgrade) using the moss species prepared at the same way and expose during the same periods (Aničić et al., 2009a; 2009c; Vuković et al., 2016). Observing 2-month exposure periods, the median concentrations of some PTEs recognised as traffic-related and toxic (Ba, Cr, Cu, Fe, and V) (Pant and Harrison, 2013), in both moss species exposed in the commercial vineyard were in the range of those concentrations in mosses exposed in the urban background sites (Vuković et al., 2016) (Figure 5.2.3a, b). In addition, the increased Cu concentrations (>20 mg kg^{-1}) in the first 2-month exposure period (1M2) in the vineyard, were even above the Cu concentrations in mosses exposed at the crossroads in Belgrade urban area; while the Cu concentrations in the exposed mosses were strongly decreasing in the following 2M2 and 3M2. This significant variation of Cu concentration in the moss through the grapevine season was probably not related to the traffic activities (Grigoratos and Martini, 2015) from the nearby road, it was rather related to the Cu-based fungicides application at the beginning of the grapevine development (Gimeno-García et al., 1996; Wightwick et al., 2008). The concentrations of the other PTEs, such as Pb and Zn, in mosses exposed in the commercial vineyard, were lower than those obtained in the mosses exposed in the city of Belgrade (Vuković et al., 2016). Probably, the soil in the

vineyard was historically less contaminated by the Pb emissions from gasoline than the soil in the city area. Observing the measured REE concentrations, lower enrichment of the studied moss species was obtained in the vineyard than in the urban city area (Vuković et al., 2016) (Figure 5.4.3a,b), which was probably influenced by the modern technological REE sources in urban areas.

The results obtained in this experiment for M4 and M6 moss exposure periods were also comparable with the results from experiments performed in the urban area in Serbia (Aničić et al., 2009a; 2009c) exposing *S. girgensohnii* for 4 and 6 months (Figure 5.4.3c). The median of Cu concentrations in the moss bags exposed 4-months and 6-months were measured in higher values in the vineyard area than in the urban area. For Al, Ba, Cd, Co, Cr, Fe, Ni, Pb, Sr, V and Zn in mosses the concentrations were in the same range with those measured in the urban background study in Belgrade (Aničić et al., 2009c). The most of measured REE concentrations in the mosses exposed in the commercial vineyard were in the same range with the REE measured in the moss exposed in urban background area (Aničić et al., 2009c), except Dy and Ga which concentrations were measured in higher values in the vineyard ambient (Figure 5.4.3c). In *S. girgensohnii* exposed during 6 months, the Sb and V concentrations in the vineyard were far below those in the urban area (Aničić et al., 2009c) while the Fe concentrations were similar to the concentrations measured in the urban ambient. However, Sb and V, specific tracers of traffic emission (Grigoratos and Martini, 2015) and fossil fuel combustion (Pacyna and Pacyna, 2001), are more typical for urban ambients. Observing REE enrichment in 6-month exposed moss, the moss material in the vineyard was more enriched by Dy and Eu than exposed moss in the urban ambient (Figure 5.4.3c).

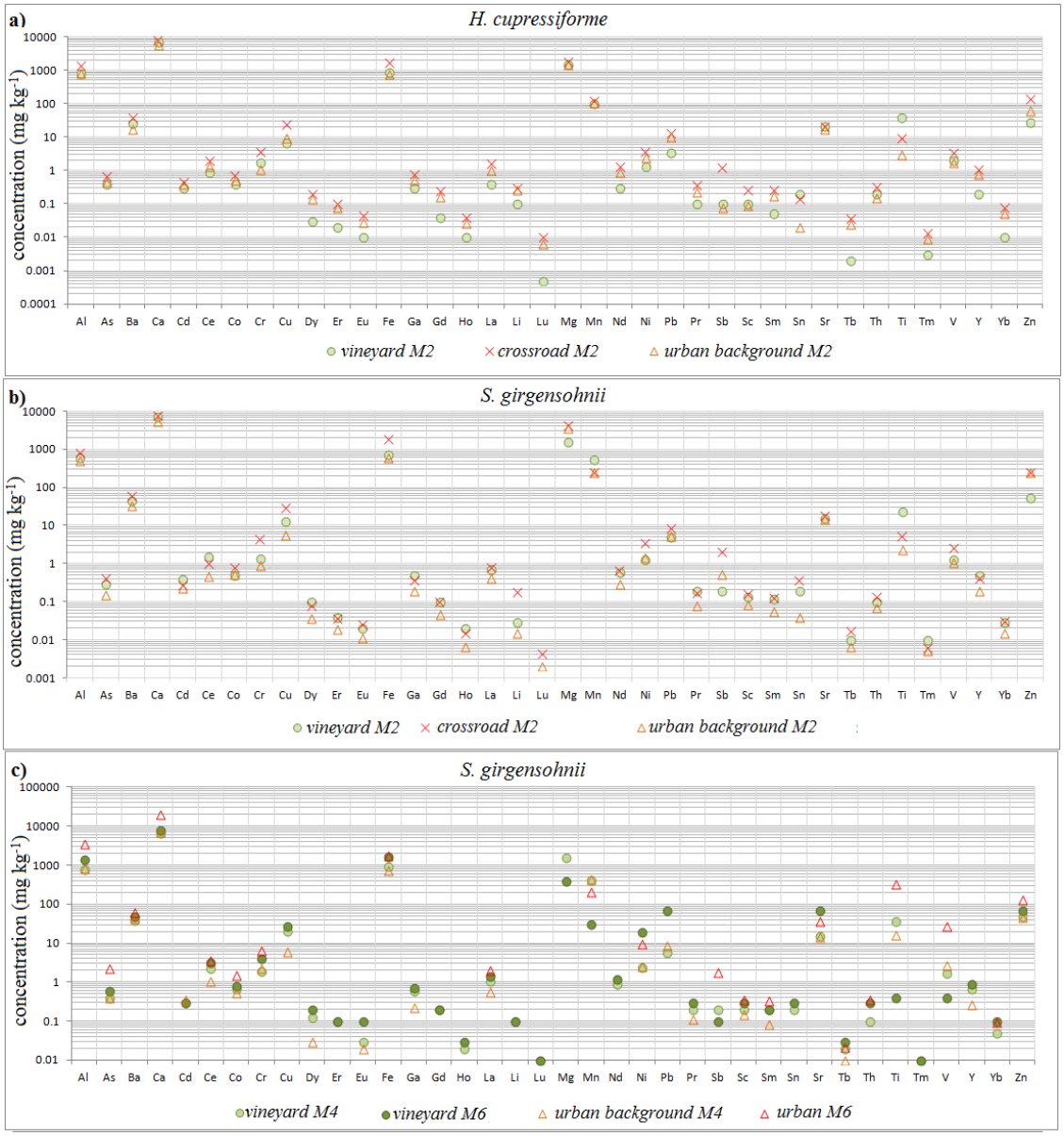


Figure 5.4.3 Median concentration (mg kg^{-1}) of the PTEs in *S. girgensohnii* and *H. cupressiforme* exposed in the commercial vineyard versus the comparative concentrations for the urban area exposed for: a) and b) 2 months (M2) (Vuković et al., 2016); and c) 4 months (M4) and 6 months (M6) (Aničić et. al. 2009a; 2009b) (Milićević et al., 2017b).

According to the discussed and compared moss bag biomonitoring performed in different ambients, it could be pointed out that in the presence of dominant PTE pollution source, the moss will give a "signal" of pollution. In this experiment, the strong "signal" of As, Cr, Cu, Ni, Fe and V were observed in the mosses for all exposure periods because of the presence of specific pollution sources. If there is not dominant emission source, the moss response to the element concentrations (Ba, Cd,

Mg, Mn, and Sr) becomes less reliable in terms to the fine spatio-temporal distribution of the concentrations (vineyard *vs.* urban background).

Finally, 2-months moss exposure period could be appropriate for receiving a reliable "signal" of the PTEs enrichment in the agricultural ambient (vineyard), especially for the PTEs present in high quantities in the vineyard ambient. The results from this experiment imply that in the first 2-month exposure period, covering the most dynamic vegetation period for the grapevine development (from 20th March to 20th May), the agrochemical treatments were the most frequent which was also indicated in Experiment 3 and this information was confirmed by personal communication with viticulturists (2015). In the case of comparable regional studies, the 6-months period which covers all the investigated vineyard season could be a pragmatic choice for the moss exposure reflecting the air pollution more representatively.

5.4.2. *S. girgensohnii* versus *H. cupressiforme* PTE enrichment

Observing the literature based on the moss bag biomonitoring studies, *S. girgensohnii* has been the most recommended because it has a high capacity to entrap higher PTE concentrations than the other moss species (González and Pokrovsky, 2014), but worldwide it is usually protected endemic species (Directive 92/43/EEC). Hence, various other moss species have been studied as an appropriate alternative to *S. girgensohnii*. The most specific for moss bag biomonitoring beside species-specific morpho-physiological features is the initial PTE concentration measured in unexposed moss, which is the most important for assessing the PTEs enrichment during the exposure (Culicov and Yurukova, 2006; Di Palma et al. 2016). In this experiment, the PTEs enrichment capacity was significantly ($p<0.05$) different between the studied mosses *S. girgensohnii* and *H. cupressiforme*, and also between different exposure periods. Only for Ba, Cd, Mg, and Sb concentrations, not significant differences between *S. girgensohnii* and *H. cupressiforme* were observed. Comparing three consecutive 2-month periods (1M2, 2M2 and 3M2), higher RAFs of most of the measured PTEs were observed in *S. girgensohnii* than in *H. cupressiforme*, exceptions were RAFs for Co, Gd, Lu, Ni, Pb, Sc, Tb and Yb (Figure 5.4.4, Table 8.5.1, Appendix 5). Although that both moss species studied in this experiment were collected in the presumable background areas, the initial PTE concentrations in *S. girgensohnii* was

lower than in *H. cupressiforme*, which probably caused higher relative element enrichment in *S. girgensohnii*, and the exceptions were the concentrations of Co, Ni, Pb and Tb. With the prolongation of the moss bag exposure time from 2-months (M2) to 6-months (M6), for both studied mosses the trends of the PTEs enrichment were similar (Figure 5.4.4, Table 8.5.1, Appendix 5). Finally, in both exposed mosses the PTEs "signal" similarly changed with the exposure time (Figure 5.4.4).

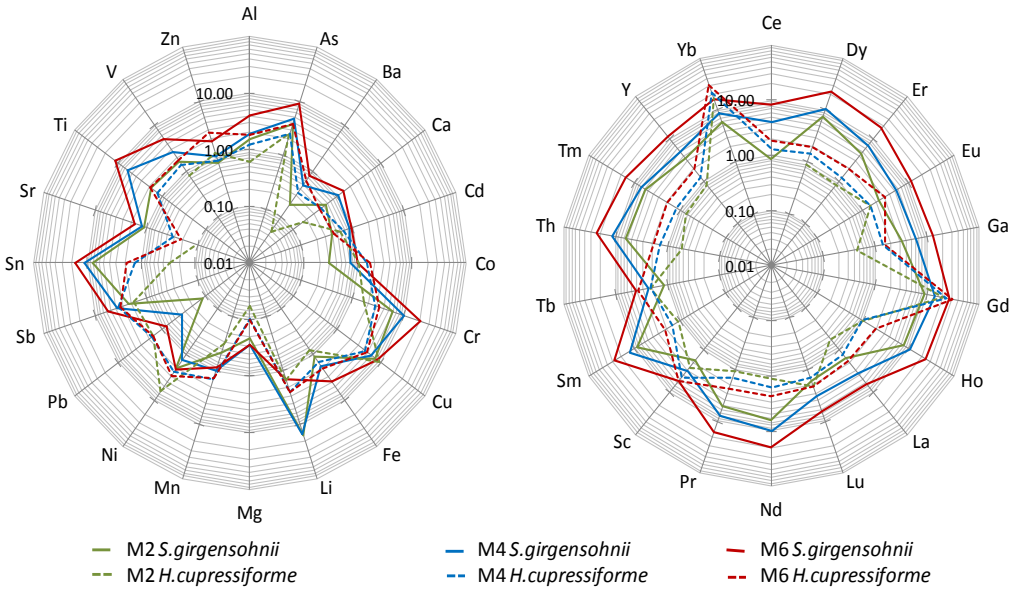


Figure 5.4.4 RAFs of the PTEs in *S. girgensohnii* and *H. cupressiforme* calculated for M2, M4 and M6 (Milićević et al., 2018b).

According to the correlation analysis which was applied in order to examine correlations between the PTE concentrations in the mosses exposed during the investigated periods (M2, M4 and M6), the significant ($p<0.05$) correlations were noticed for the concentrations of Cr (R=0.70), Cu (R=0.56), Sb (R=0.63) and Ti (R=0.76) between the investigated moss species (Table 8.5.2, Appendix 5). The significant correlations of Cu, Cr and Sb were also noticed in the experiments conducted in the urban area in Serbia (Vuković et al., 2015b; 2016), which promote an interchangeable use of *S. girgensohnii* and *H. cupressiforme* for biomonitoring of these PTEs in the investigated ambients (agricultural and urban). The same element pairs which concentrations were correlated within the species (Table 8.5.2, Appendix 5) imply that both studied moss species had a similar response to PTE concentrations present in the ambient and probably indicating the similar origin of the elements. The

pairs include Al, As, Ca, Co, Cr, Fe, Ni, V and Ti which are probably associated with the soil which could represent a diffuse PTEs source in the agricultural ambient (WHO, 2006; Viana et al., 2008). As previously explained in Experiments 1, 2 and 3, the geogenic elements in soil (e.g. As, Cr, Ni and Pb) and soil long-term use for agricultural (agrochemical treatments) represent a significant source of these PTEs and could cause the described correlations between these element concentrations. Two elements, Cu (for both species) and Ni (for *H. cupressiforme*), were not in correlation with the others, which was possibly related to some specific pollution sources, for example, the pesticides and fertilisers treatments, respectively (Thomas et al., 2012). Additionally, all measured REE concentrations in the investigated periods of the moss bag exposure have a significant correlation each to other (R>0.7; $p<0.01$) (Table 8.5.3, Appendix 5). Comparing to the conclusions for the experiment performed in the urban ambient, where *S. girgensohnii* showed as more sensitive specie than *H. cupressiforme* moss (Vuković et al., 2015a, 2016), the PTEs enrichment in both studied moss species was similar in the vineyard environment. Finally, it can be concluded that *H. cupressiforme* could be comparable (Figur 5.4.5) to dominant species in the elements capture *S. girgensohnii* (Ares et al., 2012).

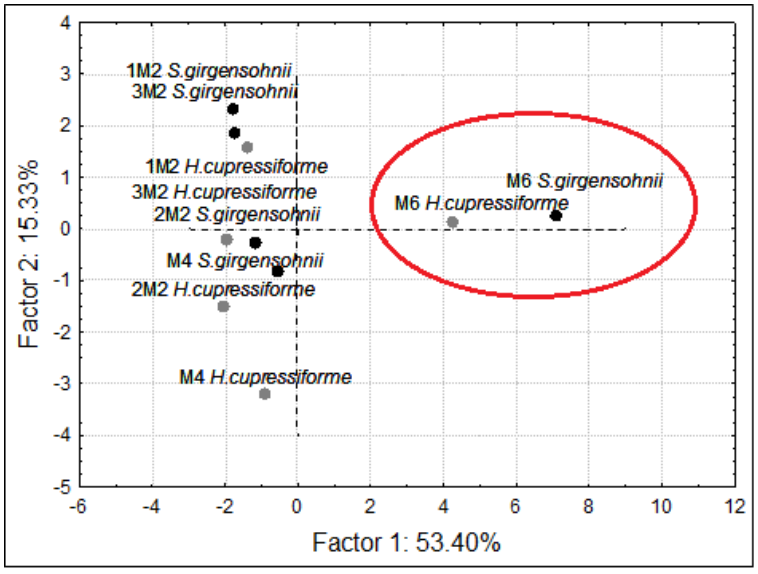


Figure 5.4.5 PCA obtaining the associations between *S. girgensohnii* versus *H. cupressiforme* exposed during different periods in the vineyard ambient.

5.4.3 Variation the moss PTE concentrations across the vineyard as a potential diffuse pollution source

In the *S. girgensohnii* and *H. cupressiforme* moss samples, the measured PTE concentrations were uniform across the studied parcels, an exception was the parcel VI (located near the metal foundry) (Figure 3.3). The concentrations of Cr, Co, Ni and Fe in mosses exposed in VI parcel were higher than the concentrations in the moss samples from the other parcels (marked by ellipses in Figure 5.4.1). Observing the literature, Cr could originate from the anthropogenic sources, such as metal smelters and metal finishing and Co could originate from metal processing industries; Ni and Fe can originate from some smelting furnace processes for the production of steel and various alloys (Kabata-Pendias and Mukherjee, 2007). Finally, enrichment of these PTEs in the mosses exposed in the parcel VI imply the possible influence of the foundry activities on air pollution in this vineyard parcel.

Only the concentrations of Sb were decreasing in the both studied mosses which were exposed moving from the road along transects through the parcels I–II–III and IV. The highest measured concentrations of Sb were obtained in both the soil samples (Experiments 2 and 3) and moss collected from the first sampling sites (Maximum Sb concentrations in Table 8.3.1, Appendix 3 and Table 8.4.2, Appendix 4), which are the closest to the nearby highway road (assigned by the rectangles in Figure 5.4.1). Conversely to the other parcels, Sb concentrations in the mosses were homogenous in the parcel VI along transect. The parcel VI is located near the foundry, which probably suppresses the traffic influence. Abrasion of Sb-containing brake linings of vehicles represents one of the most common Sb anthropogenic sources in the environment (Grigoratos and Martini, 2015).

The spatial distribution of the other measured PTEs, along the parcels' transect in the moss and soil samples from Experiments 2 and 3 (Table 8.3.1, Appendix 3 and Table 8.4.2, Appendix 4), was uniform. Finally, because there were not present point or line pollution sources, vineyard could represent a diffuse (area) pollution source of PTEs (WHO, 2006; EEA, 2007) including agrochemical treatments and polluted soil resuspension.

5.4.4 Could grapevine leaves bioindicate air pollution in the commercial vineyard ambient? Grapevine leaves concentrations versus moss concentrations

According to the results obtained in Experiment 3 (Milićević et al., 2018b), significant ($p<0.05$) correlations between Cr concentration in the leaf from May (leaf set phase) and July (veraison phase) and its concentration in the moss bag samples exposed in the vineyard during 2- and 4-month periods: Cr in the leaf in May *vs.* Cr in the moss bag after 2-months exposure: R=0.43; Cr in the leaf in July *vs.* Cr in the moss bag after 4 months of exposure: R=0.52; $p<0.05$. Additionally, the concentration of Co in the leaf samples collected in July and its concentration in the moss bag samples exposed for 4 months significantly ($p<0.05$) correlated (R=0.53). Therefore, it could be assumed that the grapevine leaves collected one month before harvest (when the agrochemicals were not using anymore; *personal communication*, 2015) could indicate ambient Co and Cr pollution in the vineyard environment. Observing the previously mentioned correlations between Co and Cr concentrations in the leaves and the concentrations in the moss bags exposed in the commercial vineyard through the grapevine season, the grapevine leaves could be promoted as a potential bioindicator of the air pollution by PTEs (e.g., Co and Cr) in the vineyard ambient.

Finally, the results from this experiment were published in the international journal *Ecotoxicology and Environmental Safety* (Manuscript: *Assessment of species-specific and temporal variations of major, trace and rare earth elements in vineyard ambient using moss bags;* Milićević et al., 2017b). Furthermore, the attention was directed to investigation of the soil, plant and air pollution by PTEs in the organic vineyard ambient where is production organised without typical application or with the negligible quantity of the conventional agrochemical treatments (Experiment 5). Further, the investigations in the organic vineyard will be compared with the investigations performed in the experimental and the commercial vineyard (experimental−Experiment 1 and commercial−Experiments 2, 3 and 4).

5.5 Experiment 5: Is soil−plant−air system in the organic vineyard less polluted than in the commercial vineyards?

5.5.1 Soil from the organic vineyard

5.5.1.1 Element concentrations

The soil samples from the organic vineyard were neutral to low alkaline (pH-H_2O (ranged from 6.90 to 8.90); pH-KCl (ranged from 6.97 to7.58) with low OM content (ranged from 0.37 to 1.90%) and high CEC (ranged from 25 to 40 cmol kg^{-1}). The descriptive statistic of the element concentrations obtained in O soil layer, A (topsoil) layer and subsoil (control) samples are presented in Table 8.6.1, Appendix 6. The concentrations of measured PTEs were lower than MAC values prescribed by the national and international regulations (Official Gazette of Republic Serbia, 2010; EU Council Directive 86/278/EEC). The obtained concentrations of Cr and Ni were around the MAC values (Table 8.6.1, Appendix 6), but they were lower in all the analysed soil depths than their concentrations obtained in Experiments 2 and 3 conducted in the commercial vineyard (Milićević et al., 2018a, 2018b), but in higher than those concentrations obtained in the experimental vineyard described in Experiment 1 (Milićević et al., 2017a) in Serbia. Additionally, the concentrations of these elements were in the significant correlation with the various elements concentrations (Cr−Al, Cr−Fe, Cr−Mg, Cr−K, Ni−Al and Ni−Li) (Table 8.6.2, Appendix 6) which represent the most important natural soil substrates (Kabata–Pendias and Mukherjee, 2007). Moreover, there were not obtained significant differences between these two elements concentrations between the studied soil layers. Thus, it seems that Cr and Ni in the organic vineyard mostly have a geogenic origin which is in accordance with many previous investigations of the different soils across Balkan Peninsula (Ličina et al., 2016; Dangić and Dangić, 2007; Salminen at al., 2005) and discussed previously in Experiment 1 and Experiments 2 and 3 (Milićević et al., 2017a, 2018a, 2018b).

5.5.1.2 Element mobility in the soil

Assessing efficiency and selectivity of the element extractions among the nine single extraction procedures, the most efficient extractants were 0.05mol L^{-1} Na_2EDTA and 0.44 mol L^{-1} CH_3COOH (Tables 7.6.3, 7.6.4 and 7.6.5, Appendix 6). Complexing agent Na_2EDTA was shown as the most efficient extractant in this experiment as well as

in the previous experiments conducted in the experimental vineyard during harvest (Experiment 1), commercial vineyard during harvest (Experiment 2) and entire grapevine season (Experiment 3) in Serbia. Percentages of the PTE concentrations extracted by the nine different extractants *vs.* pseudo-total element concentration imply that the highest MF% of Co, Cu, Fe, Pb, Sb and Zn were extracted by Na_2EDTA (Table 8.6.5, Appendix 6). This extractant has proven to be the most effective and selective for the PTEs extraction (Inczédy, 1976), as it was observed in previous experiments. However, 0.44 mol L^{-1} CH_3COOH extracted the highest concentrations of Al, B, Be, Cd, Cr, Mn, Ni and P probably because of the extractant acidity and its aggressive influence on carbonates which predominantly fix Cd and Mn in soil (Kabata–Pendias and Mukherjee, 2007) but also could make bonds with other PTEs.

Further, efficiency and selectivity between the extractants that have the similar chemical composition or molarities were compared. The deionised H_2O extracted low concentrations of only the most water-soluble PTE fractions from the soil. Moreover, the prolongation of the extraction time (from 2 to 16 h) with deionised H_2O on this soil type did not have more effective extraction influence. Comparing the chloride salts even their molarities are note equal, more efficient for the extraction of macro elements (Ca, Mg. Al and K recommended for the soil CEC assessment) from the soil were 0.1 mol L^{-1} $BaCl_2$, but it was not suitable for extracting some of the microelements. Additionally, 0.01 mol L^{-1} $CaCl_2$ could not be the most effective for extracting all the obtained elements, because Ca content could make an interference during determination (Hooda, 2010), but it could be appropriate for extracting some of the PTEs from the soil (e.g., Al, Fe, Ni, V and Zn). The weak salt solution NH_4NO_3 extracted the highest concentrations of Ba, Ca, K, Mg and Sr (Table 8.6.4, Appendix 6). Comparing extractants based on Na-salt of the NO_3^-, weak salt solution (0.1 mol L^{-1} NH_4NO_3) was more efficient for extracting most of the determined elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Si, Sr and Zn), but for extracting B, Be, Cd, Co, Pb and V more effective was $NaNO_3$ (Table 8.6.4, Appendix 6). The efficiency of NH_4NO_3 for extracting the elements from the soil was probably caused by NH_4^+ that could bound complexes and induces the additional release of these elements from the soil (Hooda, 2010).

5.5.1.3 Environmental implications in the soil

Biogeochemical index (BGI). To compare the concentrations in O soil layer with concentrations in A soil layer, BGI was calculated (Table 8.6.6, Appendix 6). The median BGI values for most of the elements indicated that there were not high PTEs sorptions in the O layer (<1 or ≈1; Table 8.6.6, Appendix 6; Figure 5.5.1). Thus, there was not frequent anthropogenic influence on O layer. Otherwise, as previously mentioned the soil of the Balkan Peninsula is enriched by As, Cr, Ni and sometimes Pb (Ličina et al., 2016; Dangić and Dangić, 2007; Salminen at al., 2005). Thus, most of the obtained PTEs in the organic vineyard probably have a geogenic origin. Only the concentrations of B, Na, S and Si had high BGI values (Figure 5.5.1) probably because of the application of some natural fertiliser quantities that are containing these elements. Comparing with the other studies conducted in the agricultural area, BGIs obtained for the elements in the organic vineyard (Table 8.6.6, Appendix 6) were lower than those calculated for the forest and the grassland soils (Mazurek et al. 2017).

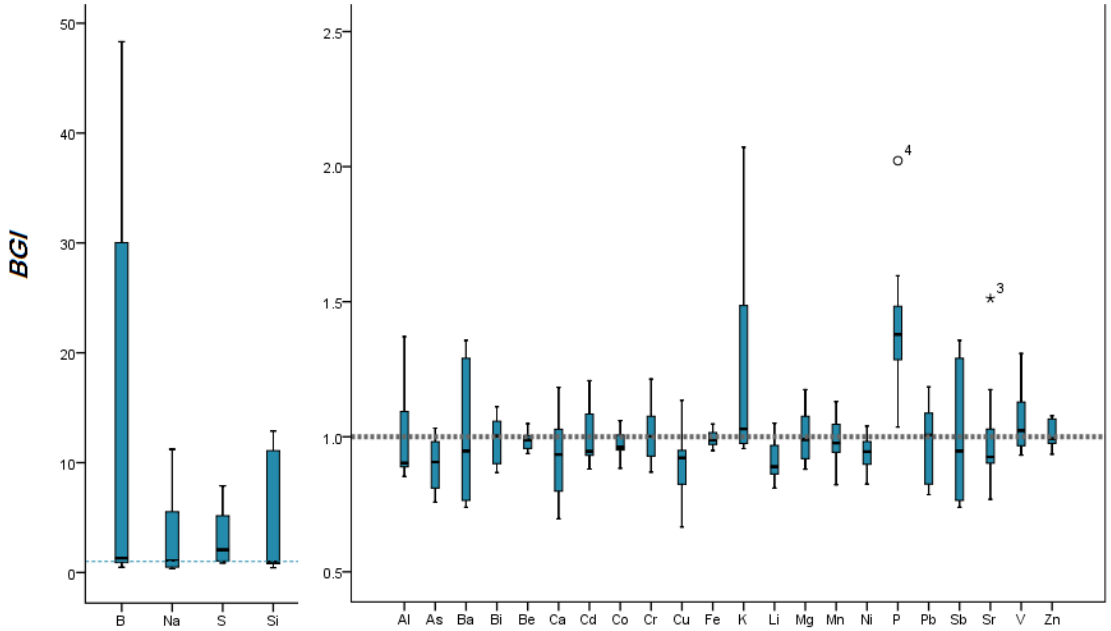


Figure 5.5.1 BGI (-) calculated for each of the measured element concentration in O soil layer; the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values; "○" represent outliers and "*" represent extremes.

Contamination factor (CF) and pollution load index (PLI). To investigate whether there any environmental implication caused by the PTE concentrations in the O and A layers in the organic vineyard, the CFs were calculated (Table 8.6.7, Appendix 6). For both O and A layers the CFs were low or moderate (CF<1 or 1<CF<3; Table 8.6.5, Appendix 6; Figure 5.5.2a), except for B in the soil collected in July when CFs were very high in the O soil layer (Figure 5.5.2.b; the red circled are the CFs obtained for the soil collected in July). Thus, even the grapevine was not treated with commercial pesticides, in the organic vineyard, B could originate from the neighbour parcels where B-based pesticides (Borax) had been used (Kabata–Pendias and Mukherjee, 2007).

In addition, PLIs for all the investigated parcels in the organic vineyard were low (PLI≈1) (Table 8.6.7, Appendix 6; Figure 5.5.2a). The PLI values in A layer (0−30 cm) were similar or slightly higher than the values obtained for the topsoil samples in Experiment 1−experimental and Experiments 2 and 3−commercial vineyards in Serbia (Milićević et al., 2017a, 2018a, 2018b). In accordance, the SOM algorithm was applied in propose whether any differences exist between PLI indices depending on the vineyard ambient, identified only two clusters of the particular samples as represented by SOM resulting map, neighbour distance plot and dominant blue circles in contrast to the light blue and yellow ones (Figure 5.5.3a,b,c). The result implied that no distinction exists between the burden of soil samples by PTEs in the organic and the commercial (Experiment 3) vineyards (Figure 5.5.3a,c). The exceptions were PLI values for the samples (25, 43, 48, 77 and 78) in light blue circles and the samples (26 and 80) in yellow circle (Figure 5.5.3c). The samples with PLI which differ from other are the nearest samples to the metal foundry from parcel VI, which were collected in April, May and July (26−in yellow circle, 48−in light blue circle, 80−in yellow circle, respectively), and the other values of PLI grouped in light blue circles were for samples from V parcel collected in April and July (25, 77 and 78) (Figure 5.5.3c).

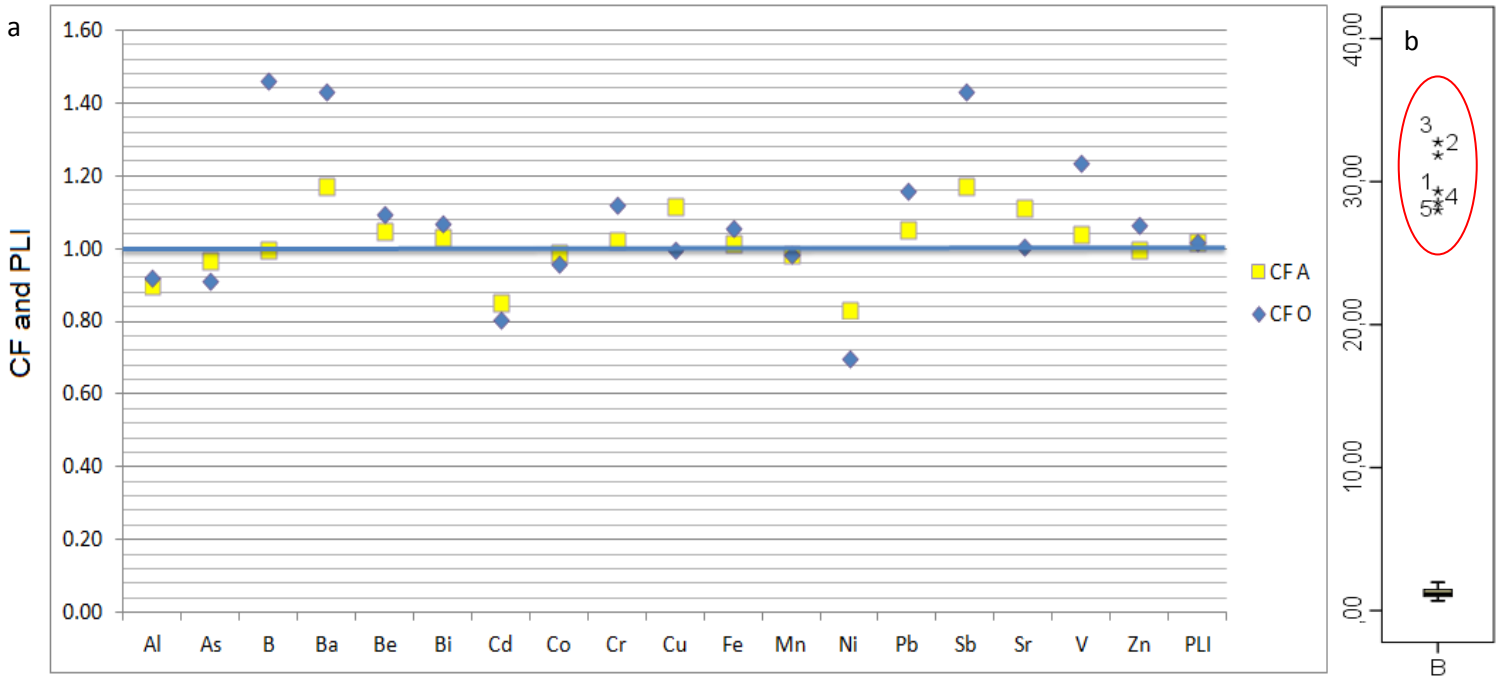


Figure 5.5.2 a) CF (-) for all obtained PTEs and the median pollution load index (PLI) values (-) in the O and A soil layers; b) CFs (-) obtained for B in all the analysed soil samples (the red circled values are the CFs obtained for the soil samples collected in July).

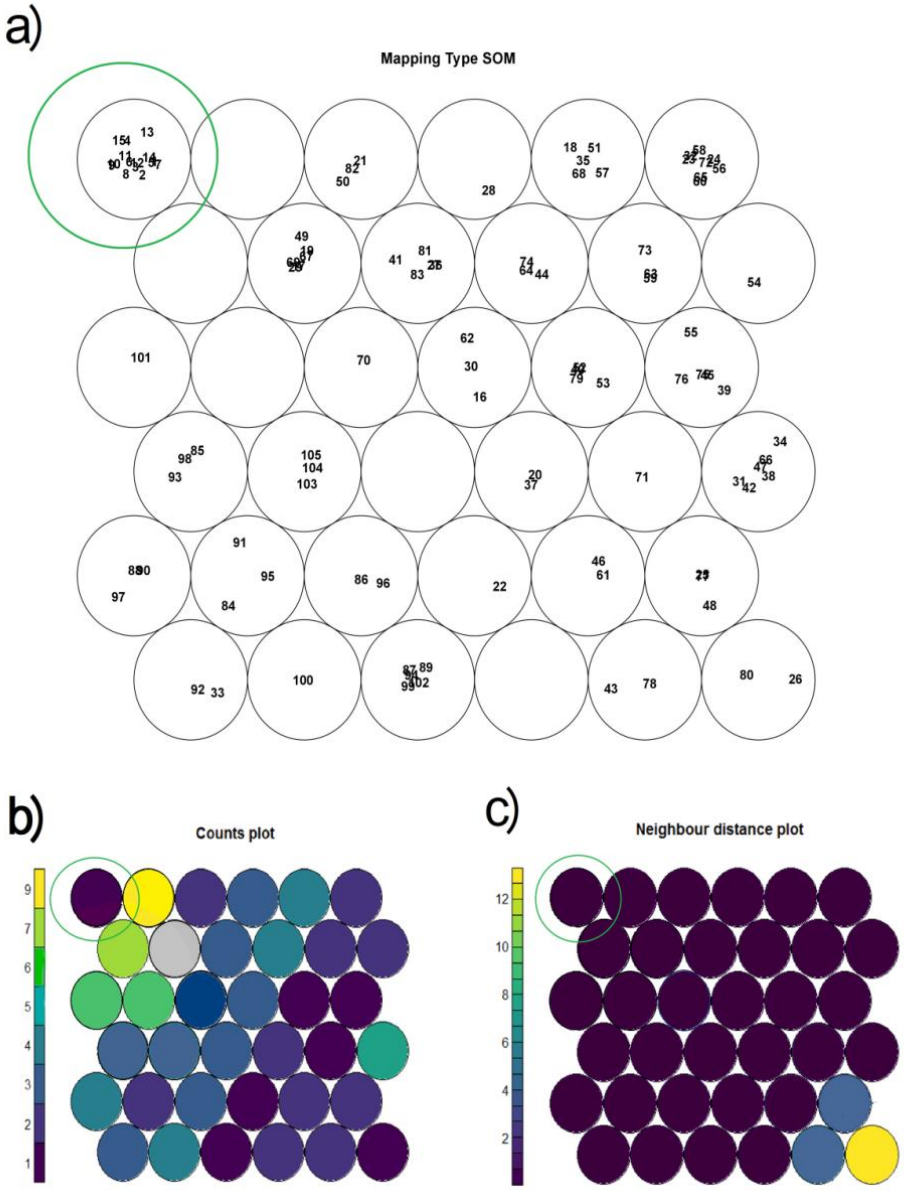


Figure 5.5.3 Self-organizing maps (SOM) classifying differences between the pollution load index (PLI) values obtained for the soil samples in the organic (green circled values 1-15) and the commercial (samples from 16 to 106) (Experiment 3; Milićević et al.. 2018a) vineyards; b) Count plots; c) Neighbor distance plot.

Environmental risk (Eri, RI). Environmental risk assessment obtained for PTEs, such as As, Cd, Cr, Cu, Ni, Pb and Zn, were<40 (Table 8.6.8, Appendix 6; Figure 5.5.4), which is defined as low (Guo et al., 2010). In addition, the highest value was ErCd (Figure 5.5.4), which indicated that the concentration of Cd, even in low concentration in this soil samples had the highest influence on the environmental risk in this soil. Moreover, according to the scale defined by Guo et al. (2010), RI (31<RI<64; Table 8.6.8, Appendix 6) in the organic vineyard was low (Table 8.6.8, Appendix 6).

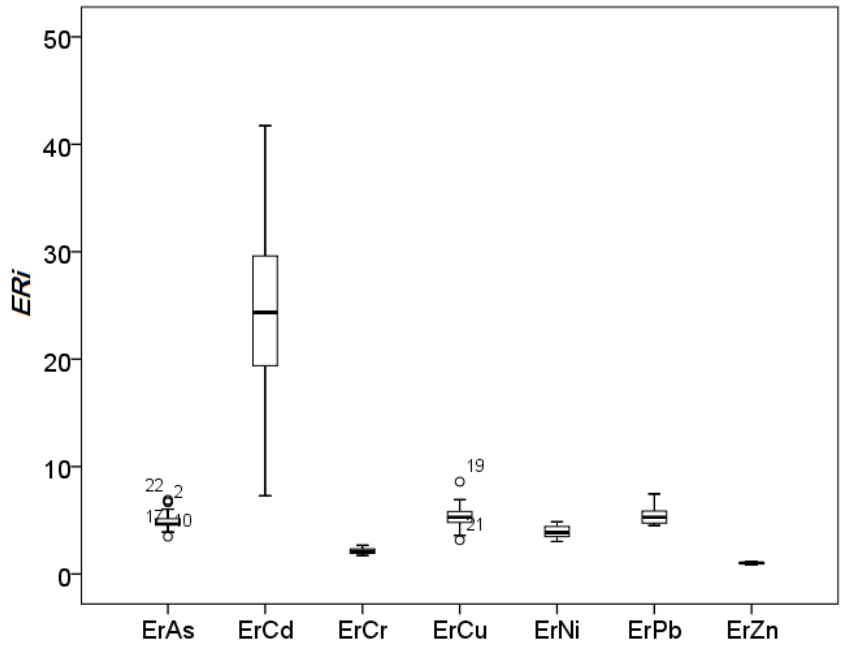


Figure 5.5.4 Eri (i=As. Cd. Cr. Cu. Ni. Pb and Zn) (-) calculated for toxic elements (As. Cd. Cr. Cu. Ni. Pb and Zn); the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values; "o" represent outliers.

Comparing the obtained results to the RI values calculated in the commercial vineyard, RI obtained for the organic vineyard soil was significantly lower (Figure 5.5.5a). Complementary to the results of Wilcoxon signed-rank test, the SOM analysis distinguished patterns of RI dissimilarity in the studied vineyards (Figure 5.5.5b,c,d). A strong difference was observed regarding the vineyard ambients as shown by dark blue circles which represent samples from the commercial vineyard (Experiment 3) in counts plot, and the lighter ones illustrating the samples from the organic vineyard (Figure 5.5.5c). Thus, the ecological risk in the organic vineyard was pointed out as significantly different (lower) than in the commercial vineyard (Experiment 4).

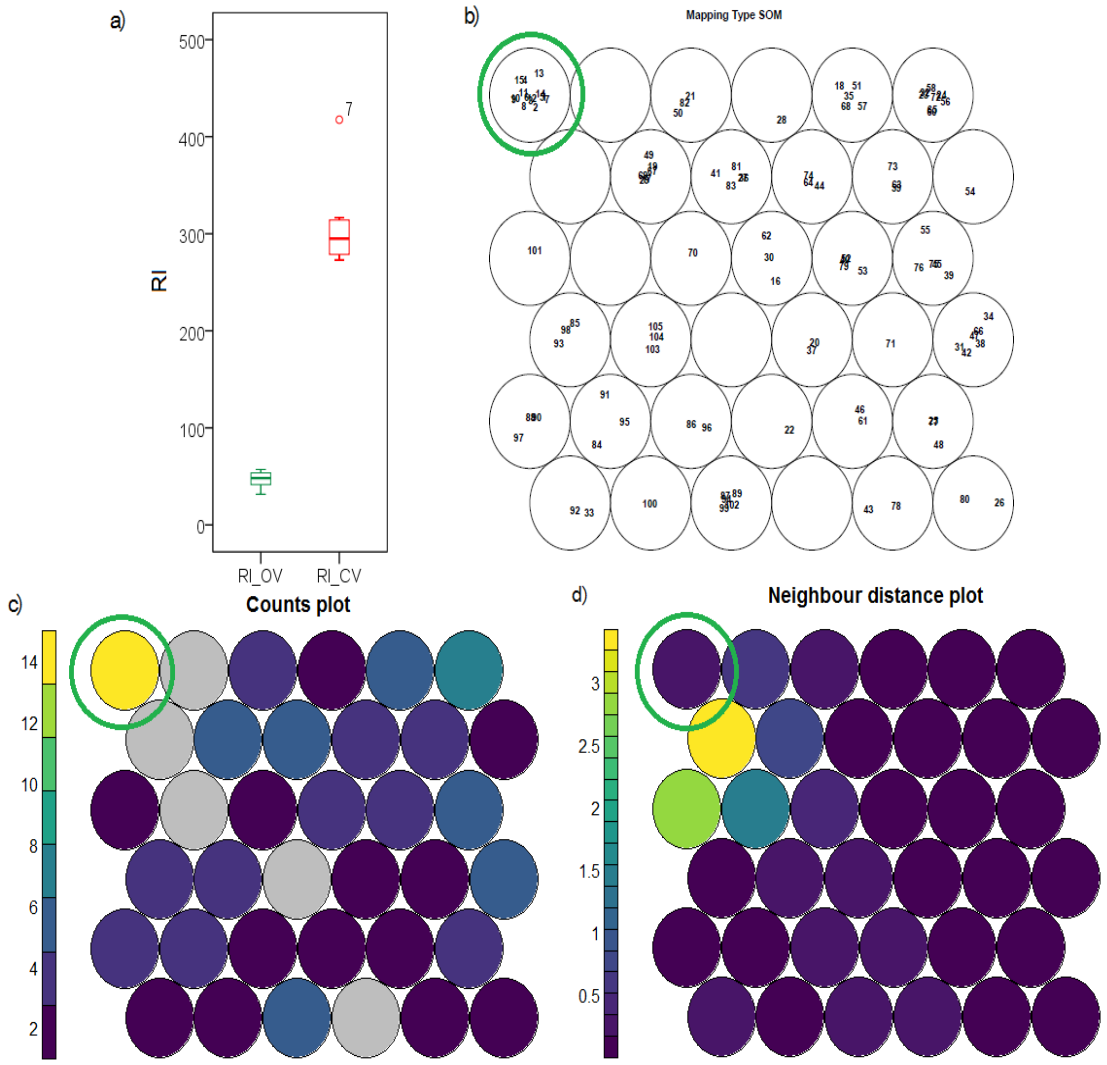


Figure 5.5.5 a) Ecological risk (RI) (-) calculated for organic vineyard (green box−plot) and commercial vineyard (Experiment 3; Milićević et al., 2018b); b) Self organising maps (SOM)-mapping type SOM observing differences between values obtained for organic vineyard (green circled values from 1 to 15) and commercial vineyard (values from 16 to 106); c) count plots SOM; d) neighbour distance plot SOM.

Bioavailability risk assessment (BRAI). Observing the calculated $BRAI_{probable}$, moderate to high bioavailability risk was noticed, while according to $BRAI_{apparent}$ low to moderate bioavailability risk was observed (Table 8.6.9, Appendix 6). Although, the total concentrations of those element applied for the BRAI calculation were lower than the total concentrations in the soil from the other investigated vineyards (Experiments 1 and 3; Milićević et al., 2017a; Milićević et al., 2018b), still the bioavailability risk was higher, which is probably influenced by the higher Cd mobility, extracted from the soil by Na_2EDTA in higher concentrations than in Experiment 3. Between $BRAI_{probable}$ and

$BRAI_{apparent}$, the significant ($p<0.01$) correlation (R=0.99) was observed, that was also proved by the regression analysis (R^2=0.97) between these values (Figure 5.5.6). Thus, as in the previous Experiment 3 where the $BRAI_{apparent}$ was developed, the significant correlation between the previously applied $BRAI_{probable}$ confirmed that $BRAI_{apparent}$ could be used as a relevant equation for the bioavailability risk assessment in the soil including a larger element set for the calculation.

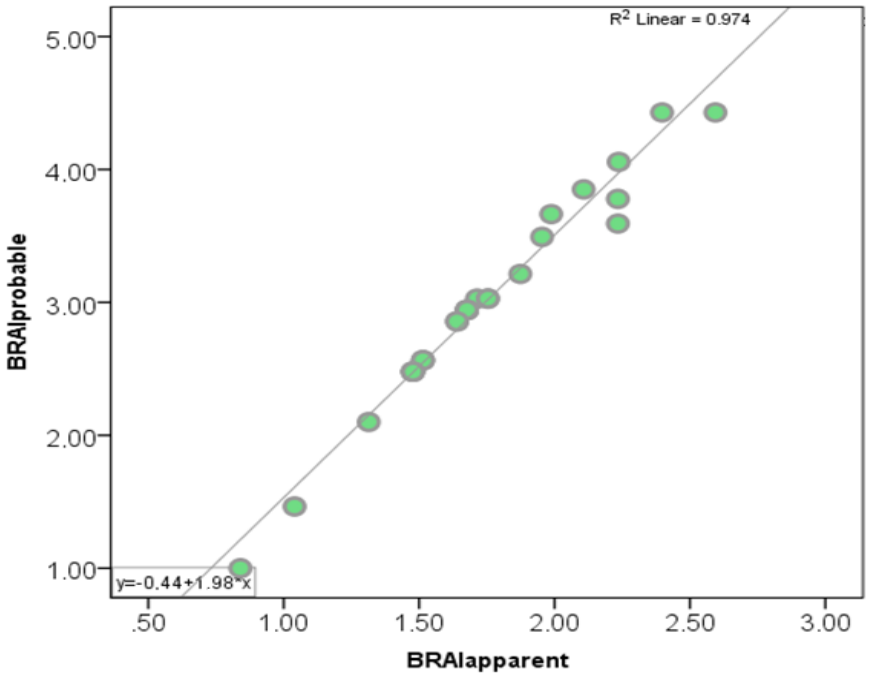


Figure 5.5.6 Regression analysis between the $BRAI_{probable}$ (-) and $BRAI_{apparent}$ (-) values obtained for the soil samples from the organic vineyard.

The obtained $BRAI_{probable}$ in the organic vineyard was higher than $BRAI_{probable}$ observed in the commercial vineyard in Serbia, while $BRAI_{apparent}$ was similar to $BRAI_{apparent}$ in the commercial vineyard (Experiment 3; Milićević et al., 2018a) (Figure 5.5.7). The median values of $BRAI_{probable}$ in the organic vineyard (the values were ranged from 1 to 2.67; Table 8.6.9, Appendix 6) were slightly lower than $BRAI_{probable}$ of the urban soil (Madrid et al., 2008), while the values were significantly lower than $BRAI_{probable}$ values for the mining areas (Anju and Banerjee, 2011), the agricultural soils (Poggio et al., 2009) and residential sites (Poggio et al., 2009).

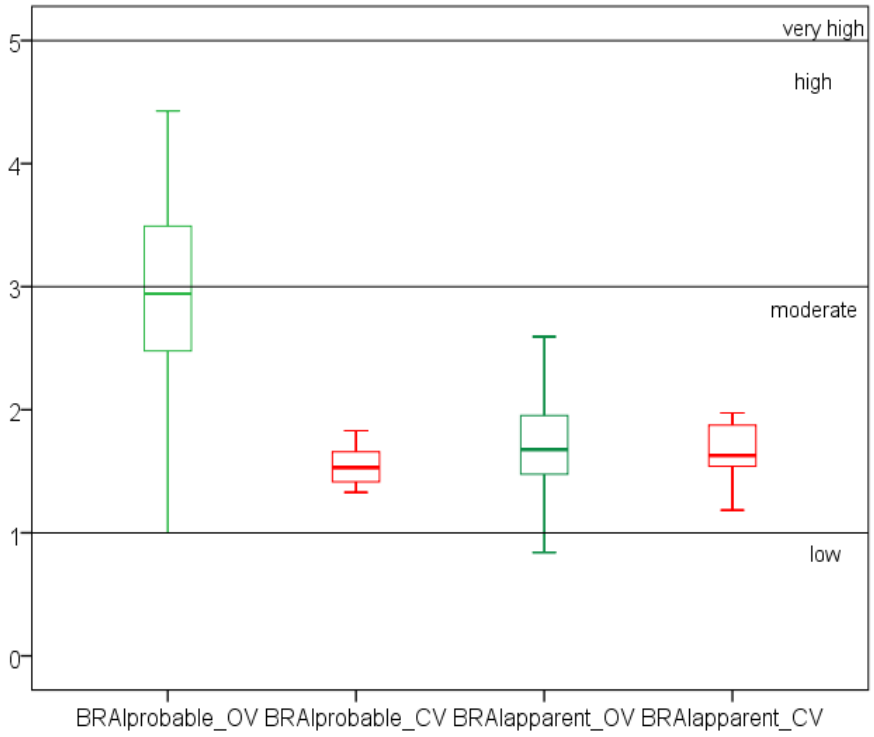


Figure 5.5.7 $BRAI_{probbable}$ versus $BRAI_{apparent}$, calculated for the organic vineyard (green box-plots) and commercial vineyard (Experiment 3) (red box-plots); the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values.

5.5.1.4 Health risk assessment for PTEs in the soil

According to applied health risk assessment calculations (Table 3.4), adjusted to simulate farmers exposure to the soil in the organic vineyard during the grapevine season (from April to October), both non-cancerogenic risk ($\Sigma HI<1$; Table 8.6.10, Appendix 6) and carcinogenic risk ($\Sigma R \leq 10^{-5}$; Table 8.6.10, Appendix 6) were low. These values were slightly lower than those obtained in Experiment 2 calculated for the field workers in the commercial vineyard (Table 8.3.8, Appendix 3), which indicated that during a long exposure time, the organic production environment could be healthier for the field workers. Otherwise, as it was observed in Experiment 2 in the commercial vineyard, in the organic vineyard the oral intake also had the highest impact on non-carcinogenic risk, which leads to further ingestion and risk for human health. The total carcinogenic risk in the organic vineyard was within the acceptable range proposed by EPA (US EPA, 2005).

5.5.2 Grapevine samples

5.5.2.1 Element concentrations in grapevine samples (leaf, petiole, whole berry, skin, pulp and seed)

The descriptive statistic of the element concentrations measured in different grape parts (seed, pulp, skin and whole berry), petiole and leaf are presented in Tables 7.6.11 and 7.6.12, Appendix 6. The element concentrations in the grapevine samples (leaves, petiole and grape berries) did not vary significantly ($p<0.05$) between the studied parcels in the organic vineyard and the grapevine varieties. Moreover, observing the concentrations of the elements measured in the outer parts of the grapevine (skin, petiole and leaf), the highest concentrations were observed in the leaves (Tables 7.6.11 and 7.6.12, Appendix 6), which imply that the leaves probably because of the plate and rough structure more efficiently entrap air deposits than the other grapevine parts, as it was also obtained in Experiment 2 conducted in the commercial vineyard. In addition, only Ba and Na were measured in higher concentrations in the petioles than in the other grapevine parts (Tables 7.6.11 and 7.6.12, Appendix 6). In accordance with the previously studied commercial vineyard where was concluded that these two elements in the grapevine parts mostly originate from the soil (Experiment 2 and 3; Milićević et al., 2018a, 2008b) it could be assumed that also in the organic vineyard these elements from the soil mostly accumulated in the petiole.

In the grapevine berry samples, the PTE concentrations were lower than the concentrations in the leaf and petiole samples (Tables 8.6.11 and 7.6.12, Appendix 6). The leaf samples in the organic vineyard had lower PTE concentrations than those measured in the leaves from those obtained in the Experiments 1 and 2, conducted in the experimental and the commercial vineyards (Table 8.2.2, Appendix 2, Table 8.3.3, Appendix 3). The national regulations of the Republic of Serbia prescribe the MAC for only a few elements in fresh fruit (grape) (Official Gazette of Republic Serbia, 2011). Accordingly, the concentrations of PTEs (As, Cd and Pb) in the grape berries (Table 8.6.11, Appendix 6) were lower than the MAC (Official Gazette of Republic Serbia, 2011). Among the grape berry parts (skin, pulp and seed), the highest concentration of the elements was determined in the grapevine seeds. Namely, the concentrations of the elements in the grapevine parts were slightly lower than those in the previously studied

varieties described in Experiments 1 and 2 (Milićević et al., 2017a; Milićević et al., 2018a).

Finally, according to the applied equations for assessing the environmental implications for the soil samples, only B and Cd had an influence on the soil contamination and bioavailability risk, respectively. According to the concentrations distribution for different grapevine parts (seed, pulp, skin, petiole and leaf), it could be assumed that the concentration of Cd had a higher influence to the inner parts of the grapevine (seed and pulp) and the concentration of B mostly had an influence to the grapevine leaves (Figure 5.5.8). Thus, these two elements obtained in the grapevine parts from the organic vineyard, probably originate from the different sources, Cd originates only from the soil and B originates from the air deposition of this element on the soil and leaves.

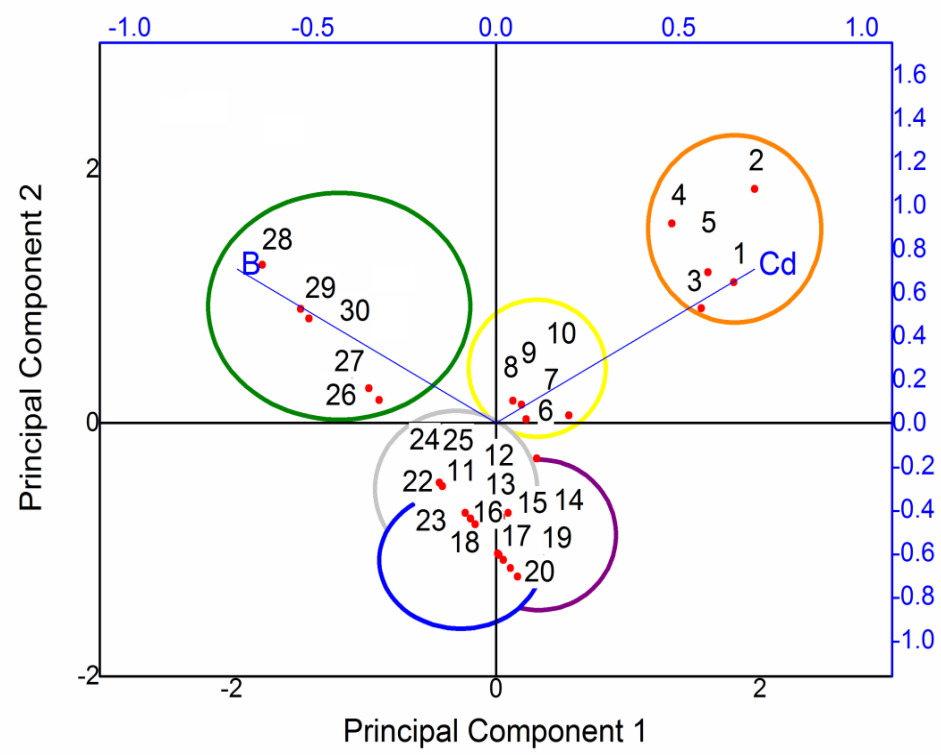


Figure 5.5.8 PCA representing the distribution of B and Cd concentrations in the different grapevine parts; seed−orange circle: samples 1−5; pulp−yellow circle: samples 6−10; skin, whole berry and petiole− a set of purple, blue and gray circles, samples: skin (11−15); whole berry (16−20) and petiole (21−25); leaf−green circle: samples 26−30.

5.5.2.2 Environmental implications of the grapevine samples (BAC and RF)

According to the calculated BACs, the studied varieties could not easily accumulate PTEs (BAC<1). Although the grapevine was not hyper-accumulating PTEs from the soil, they probably slightly accumulated some quantities of PTEs from the soil. Thus, observing BAC values, the grapevine has mostly the tendency to accumulate B, K, Mg and P (Table 8.6.13, Appendix 6) in the case of neutral to low-alkaline soil with low OM content. Moreover, all these elements are constituents of the fertilisers used in some low quantities in organic production, but also could originate from neighbour parcels. However, from these elements only B in higher concentrations could cause serious problems to the plant development and further could have slightly toxic effects to the human health (Kabata–Pendias and Mukherjee, 2007).

However, according to the calculated RFs some of the elements, (Al, As, B, Ba, Be, Cu, Mn, Mo, Ni, P, Pb, Sb, Sr, V and Zn), especially those observed in the leaf samples (Table 8.6.14, Appendix 6; Figure 5.5.9), could originate from the air deposition and remote pollution sources. According to the observed RFs of the previously tested grapevine varieties in Experiment 2 and 3 (Milićević et al., 2018a, 2018b), the organically growth grapevine leaves indicate more intensively air pollution influence than commercially growth grapes. The leaves in organic vineyard probably more intensively reflect the air deposition because of the absence of the frequent agrochemical treatments and because of the lower influence of PTEs from the soil. Thus, the initial PTEs levels in the organically grown leaves were lower than these conventionally grown.

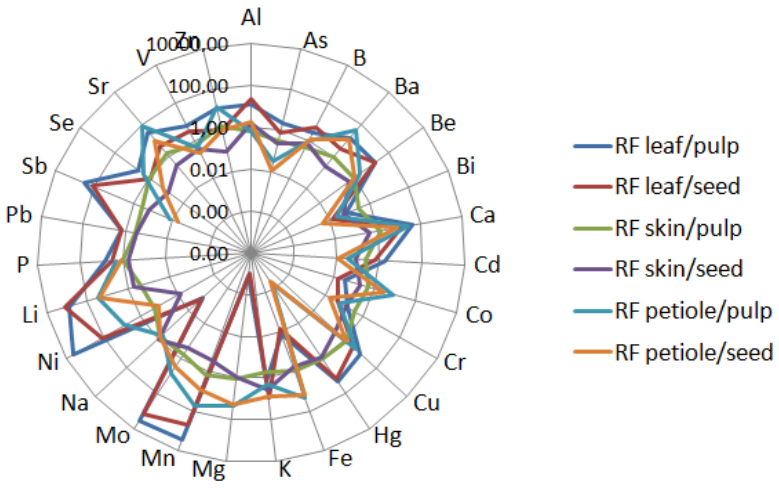


Figure 5.5.9 RF (-) calculated for the outer grapevine parts (leaf, skin and petiole).

5.5.2.3 Health risk assessment for the grape consumers

Based on the health risk assessed for the grape consumers, the non-carcinogenic risk for the human intake of organically grown grapes (adults and children) were not observed ($\Sigma HI<1$; Table 8.6.15, Appendix 6). Moreover, according to the adjustable formula for the total carcinogenic risk, it was not found for the grapevine consumers ($\Sigma R \leq 10^{-5}$; Table 8.6.15, Appendix 6). The values of the health risk indexes were lower than the health risk observed in Experiment 2, in the commercial vineyard (Milićević et al., 2018a), and thus, observing the long-term consumption, the grapevine growth in the organic vineyard could be safer for consumers.

5.5.3 Air pollution assessment influenced by PTEs using moss bag technique

The concentrations of all the measured elements in the mosses were above the LOQ_T, except for K and Na which were also pronounced in Experiment 4 and in the previous moss bag biomonitoring studies (Adamo et al., 2003; Aničić et al., 2009a; Milićević et al., 2017b). According to the element concentrations in the moss samples after 2-month exposure, reliable "signal" of PTEs was noticed (Table 8.6.16, Appendix 6) in this experiment as well as in Experiment 4. However, comparing to the other studies where active moss biomonitoring was performed during 2 months, in the organic vineyard the concentrations of most of the measured elements were significantly lower than those observed in Experiment 4, in the agricultural (commercial vineyard) and urban (the crossroad and urban background sites) areas (Figure 5.5.10a) (Vuković et al., 2016; Milićević et al., 2017b). The observed element concentrations in the moss samples exposed for 4-month period indicated that there were the lower PTE concentrations (Table 8.6.16, Appendix 6) in the mosses exposed in the organic than those exposed in the commercial vineyard (Experiment 4; Milićević et al., 2017b) and suburban area (Aničić et al., 2009c) (Figure 5.5.10b). Thus, from the aspect of the moss bag biomonitoring application in a presumably non-polluted ambient due to the absence of the agrochemical additions, a reliable "signal" of PTE enrichment ($>LOD_T$) was detected in the biomonitor after 2-month exposure. It seems that previously selected exposure time of 2-months might be kept for the future intercomparative studies with different land use classes such as urban or industrial ambient.

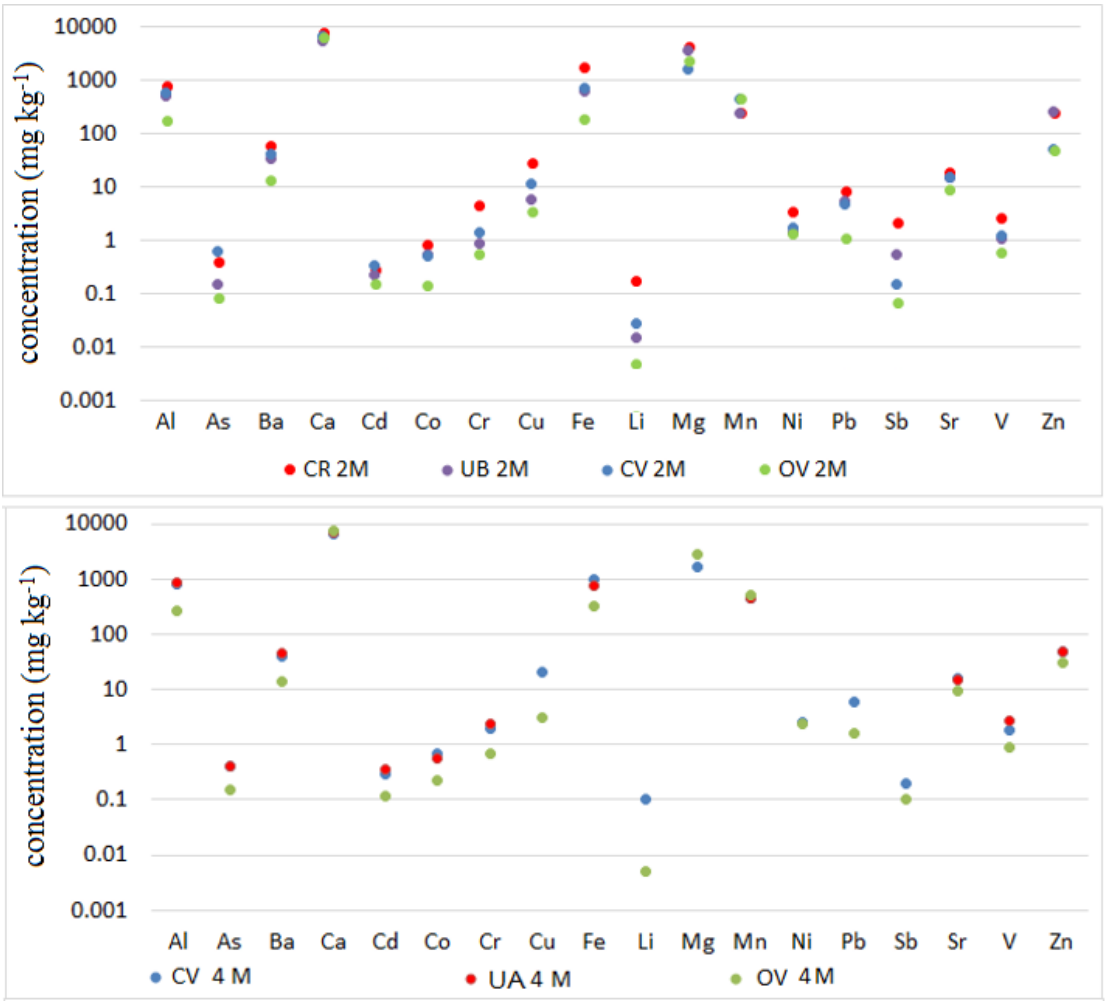


Figure 5.5.10 Median concentration (mg kg^{-1}) of the elements in *S. girgensohnii*a: a) exposed during 2 months (2M) in the organic vineyard (OV 2M) *vs*. the comparative values for commercial vineyard (CV 2M) (Milićević et al., 2018b), the crossroads (CR 2M) and the urban background (UB 2M) ambients in Belgrade (Vuković et al., 2016); and b) exposed during 4 months in the organic vineyard (OV 4M*) vs.* the comparative values from the commercial vineyard (CV 4M) (Milićević 2017b) and urban area (UA 4M) (Aničić et. al. 2009).

Because the initial concentration can influence the pollutant enrichment in moss once when it is exposed in the field, excluding the influence of initial element concentrations is specific for the moss bag biomonitoring. Hence, the previous claims about element concentrations in the moss exposed in the organic vineyard have been confirmed by the calculated RAF values (Table 8.6.16, Appendix 6), which were also lower than those observed in Experiment 4 conducted in the commercial vineyard and those obtained in the urban area in Belgrade (Aničić et al., 2009a; Vuković et al., 2016; Milićević et al., 2017b). According to the calculated RAFs, slightly higher values (RAF>1) for Al, As, B, Cd, Co, Cr, Fe, Sb, V and Zn than the values for other measured

elements were observed (Table 8.6.16, Appendix 6). In addition, RAF calculated for B was significantly higher than RAF for Cd which also implies that higher accumulation of B in moss confirmed its airborne origin in the grapevine leaves while lower moss accumulation of Cd implied that this element was not significantly accumulated from the air deposition. Observing the RAF values, the higher accumulation of some elements (Al, As, Co, Cr, Fe, Pb, Sb and V) were observed during 4-month than 2-month exposure (Figure 5.5.11), which confirms the previous observation in Experiment 4, that in the agricultural area more than 2-months could give more reliable cumulative pollution "signal" (Experiment 4; Milićević et al., 2017b). Contrary, for 2-month bag exposure the moss showed higher B, Cd and Zn enrichment. As it previously noticed, the concentrations of B were also increased in the soil O layer samples collected in July when the moss bags were exposed, as well. This period of 2-month moss exposure (from May to July) represents the grapevine growing period and probably some allowed agrochemicals were applied during this period and also these elements could originate from the neighbour parcels where some of the pesticides or fertilisers containing B and Zn were used for the treatment of the agricultural product. Comparing the PTE enrichment in moss, slightly higher RAF values were observed in moss exposed during 4 months for Al, As, Co, Cr, Fe, Pb, Sb and V than in moss exposed during 2 months, which can originate from the soil resuspension or some machine movements from the neighbourhood.

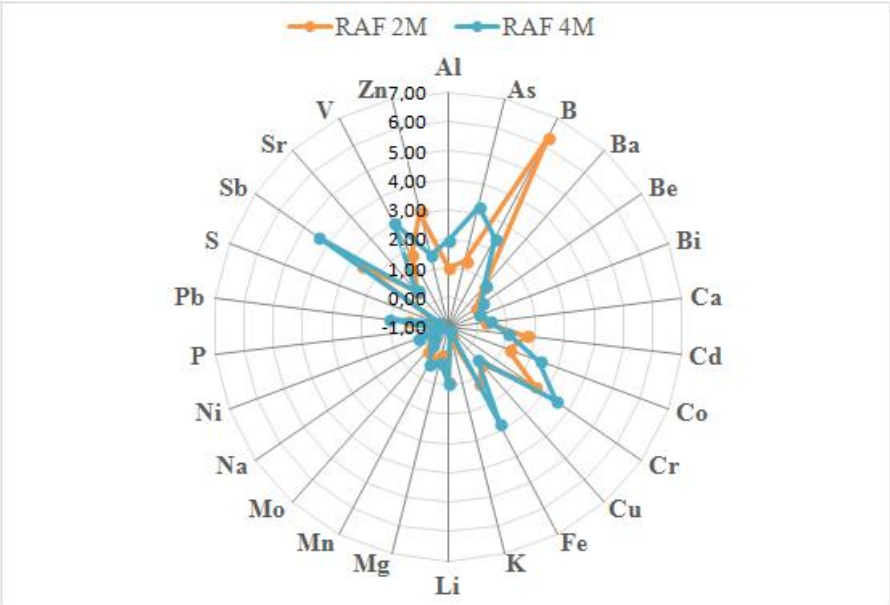


Figure 5.5.11 RAF (-) for the mosses exposed for 2 and 4 months in the organic vineyard ambient.

Finally, the results from this experiment have been submitted for the publication in the international journal. Further, on the samples collected from commercial and organic vineyards some non-destructive techniques were applied to obtained PTE concentrations and magnetic PMs. These techniques were used because of their cost-efficiency, fast performance and user-friendly (there is not a necessity for chemical digestions with strong acids). Overall, the main goal for the next experiment set up was testing magnetic parameters (SIRM and χ) as a proxy for the ambient pollution in the vineyard ambients.

5.6 Experiment 6: Magnetic parameters as a proxy for soil and leaves particle pollution in the commercial and the organic vineyards

5.6.1 Magnetic parameters in the soil and leaf samples

The measured SIRM (mass-normalised) and χ (mass-normalised) values in the soil and leaf samples are presented in Table 8.7.1, Appendix 7. The soil SIRM in the samples from commercial vineyard ranged from 721×10^{-6} μA m² kg^{-1} to 9735×10^{-6} μA m² kg^{-1}, whereas the SIRM values in the soil from organic vineyard ranged from 501×10^{-6} μA m² kg^{-1} to 2771×10^{-6} μA m² kg^{-1}. The soil χ values in the commercial vineyard ranged from 1.60×10^{-7} m^3 kg^{-1} to 3.13×10^{-3} m^3 kg^{-1} in samples while in organic vineyard values ranged from 3.25×10^{-8} m^3 kg^{-1} to 3.50×10^{-3} m^3 kg^{-1}. The mean values of both magnetic parameters (SIRM and χ) (Table 8.7.1, Appendix 7) obtained in the investigated vineyards were lower than those obtained in the soils collected from mining and smelting region (Wang et al., 2018). The soil χ values in the investigated vineyards were higher than the values measured in desert soils collected far from cultivated land and human activities and with a natural vegetation (Liu et al., 2017) and similar to the values obtained in the soils from irrigated cropping, dry-land farming and pasture area (Asgaria et al., 2018).

The measured leaf SIRM values obtained for the samples from the commercial vineyard ranged from 25×10^{-6} μA m² kg^{-1} to 178×10^{-6} μA m² kg^{-1} (Table 8.7.2, Appendix 7). The leaf SIRM values of the samples from the organic vineyard were slightly higher than those obtained in the commercial and ranged from 48×10^{-6} μA m² kg^{-1} to 237×10^{-6} μA m² kg^{-1}. The leaf χ values in the commercial vineyard ranged from -1.43×10^{-7} to 2.33×10^{-8} m^3 kg^{-1}, while in the organic vineyard leaf χ values ranged from -5.76×10^{-7} to 2.13×10^{-8} m^3 kg^{-1}. As observed by Hofman et al. (2017), who reviewed 46 published studies, the leaf SIRM values (mass-normalised) were widely ranged from 0.002 to 27.50×10^{-3} A m^2 kg^{-1}, while χ values were ranged from -0.9×10^{-8} to 846×10^{-8} m^3 kg^{-1}. Besides these ranges have shown large variabilities due to varieties in morphological characteristics of selected species, sampling location and exposure time, the leaf SIRM and χ values from the investigated vineyards were low. Comparing the grapevine leaf SIRM values with SIRM values determined in mosses (Vuković et al., 2015a), the SIRM leaf is lower than the moss SIRM, probably because the leaf surface

particle accumulation capacity appears to be lower due to the leaf smoother surfaces compared to mosses which have markedly higher surface and a phyllodes cuticle absence (Hofman et al., 2017).

Observing the obtained soil SIRM and soil χ values in the samples from two vineyards, the soil SIRM values were slightly higher for the soil from the commercial vineyard than those obtained for the samples from the organic vineyard (Figure 5.6.1a), while the higher leaf SIRM values were obtained in the organic vineyard (Figure 5.6.1b). This was in accordance to the observed results in Experiment 5 conducted in the organic vineyard where it was assumed that the leaves from organic vineyard probably rather reflected neighbour or remote air pollution due to the absence of the local foliar agrochemical application in the area.

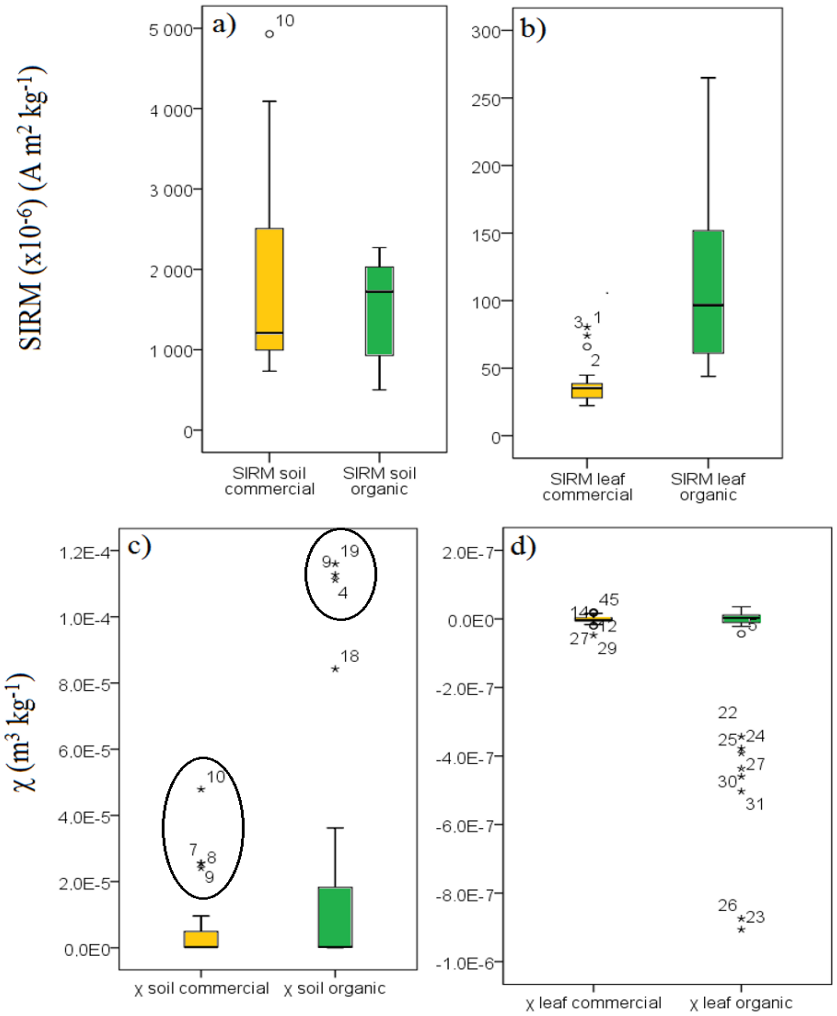


Figure 5.6.1 SIRM values ($Am^2\ kg^{-1}$) in a) soil samples, b) leaf samples and χ values ($m^3\ kg^{-1}$) in: c) soil samples and d) leaf samples from commercial and organic vineyards; orange box-plots represent results for the commercial vineyard, while green box-plots represent the organic vineyard; the middle line of the box represents the median, top and bottom represent first and third quartiles and whiskers represent maximum and minimum values; "°" represent outliers and "*" represent extremes.

The obtained χ values for both soil and leaf were measured in a similar range in both investigated vineyards (Figure 5.6.1c,d). However, soil χ values indicated some polluted samples from commercial vineyard (Figure 5.6.1c, orange box-plot, circled) parcel (parcel V; Figure 3.3) located near the highway road. In addition, observing the soil χ values in the organic vineyard (Figure 5.6.1c, green box-plot, circled) through the entire investigated season (Figure 3.4), χ values indicated that the parcel 4 is potentially polluted probably because of its position (near the Danube River and not surrounded and protected by the trees and shrubs barrier) (Figure 3.4) so some remote air pollution could impact the parcel.

Observing the distribution of both soil SIRM and soil χ values for the samples collected through the grapevine season in investigated vineyards (Figure 5.6.2a,b,c,d), there were not observed significant differences between the values of both magnetic parameters obtained through the grapevine season in the soil from the commercial vineyard (Figure 5.6.2a,c). However, it can be noticed that both magnetic parameters indicated some sampling sites located near the road as markedly different from other sites (Figure 5.6.2a,c) in the commercial vineyard. According to soil SIRM, in the organic vineyard, the highest magnetic PM content in the soil was observed in July contrary to soil χ values which indicate the highest magnetic PM content in samples from organic vineyard collected in August (Figure 5.6.2b,d). The values of SIRM are indicative for the concentration, composition and grain size of magnetic PM, while χ values are indicative for the concentration of magnetic PM. Thus, the diversities of SIRM and χ as a proxy for pollution could also be a consequence of the potential presence of magnetic PM with different grain size and composition which could be identified by the ratios of SIRM/χ, where higher SIRM/χ ratio indicates smaller grain size (Wang et al., 2017; Salo et al., 2017). As soil χ represent an exclusive indicator of PM levels, due to soil χ values obtained for samples from organic vineyard, the vineyard parcel 4 appeared to be more influenced by potential air deposition influence of magnetic PM in this parcel (Figure 5.6.2d). This parcel is located together with parcel 5 near the Danube River (Figure 3.4) which coastline is known for numerous crop fields and agricultural activities that could represent a remote diffuse source of dust pollution.

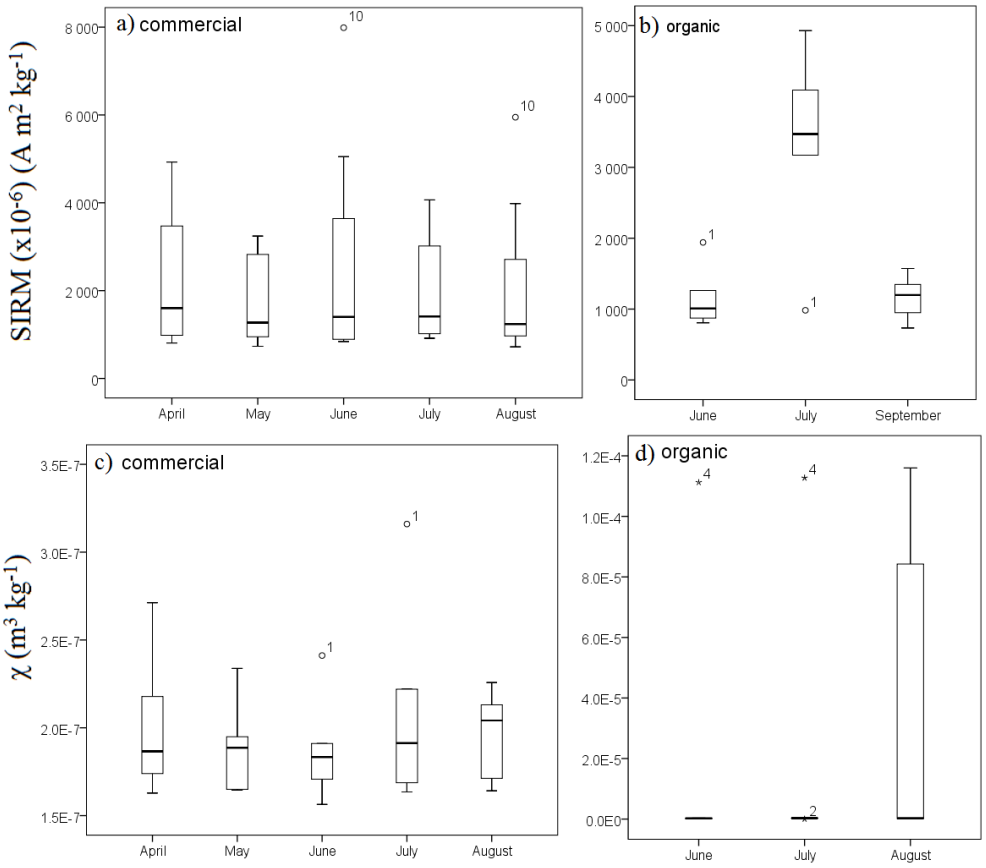


Figure 5.6.2 Soil SIRM values ($Am^2\ kg^{-1}$) obtained for samples collected through the vineyard season in a) commercial and b) organic vineyards; and soil χ values ($m^3\ kg^{-1}$) in samples from c) commercial and d) organic vineyards; the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values; "o" represent outliers and "*" represent extremes.

In parallel, observing the distribution of the leaf SIRM and leaf χ values obtained for the samples from the commercial and the organic vineyards (Figure 5.6.3a,b,c,d) only leaf SIRM indicated differences in magnetic PM levels and composition in the leaves through the season (Figure 5.6.3a,b). According to these distributions, in the commercial vineyard the highest SIRM values were observed in August (harvest period) and for some sites near the highway road (Figure 5.6.3a, circled values). In the organic vineyard, there was a prominent magnetic PM accumulation (Figure 5.6.3b, circled values) in the leaves from parcel 5 (which is located with parcel 4 near the Danube River) (Figure 3.4).

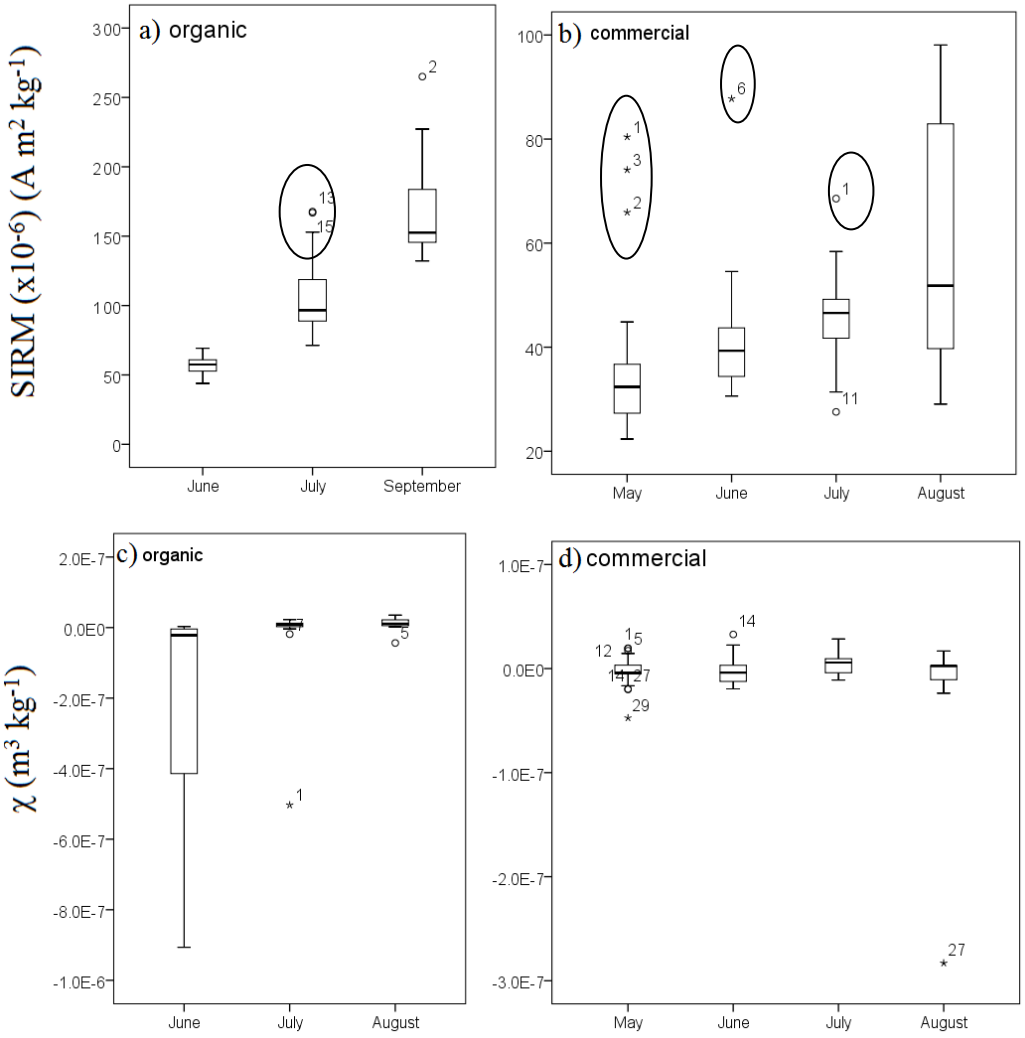


Figure 5.6.3 Leaf SIRM values ($Am^2 kg^{-1}$) obtained in samples collected through the grapevine season in a) commercial (circled samples are the leaf samples collected from the nearest sampling sites to the highway road), b) organic (circled samples are the leaf samples from the parcel 5-located together with parcel 4 near the Danube River) and χ values ($m^3 kg^{-1}$) in leaf samples from c) commercial and d) organic vineyards; the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values; "o" represent outliers and "*" represent extremes.

5.6.2 Non-destructive versus destructive method for element concentrations analyses

Pseudo-total element concentrations in the soil and total element concentrations in the leaves obtained using ICP-OES and ICP-MS (Experiments 3, 4 and 5; Milićević et al., 2018a, b) were additionally analysed with non-destructive technique WD-XRF using screening Uniquant program. It was performed in order to compare the magnetic element concentrations in these environmental matrixes with the content of the magnetic parameters in the samples indicating the air pollutants content. Finally, all

these parallel analyses were done to investigate easy-performing and faster non-destructive methods for indicative environmental pollution screening.

Applying WD-XRF, a program Uniquant which is an appropriate for screening the element content in various samples: 22 element (Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, S, Si, Sr, Ti, V, Zn and Zr) concentrations were determined in the soil samples while 16 element (Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Rb, S, Si, Sr, Ti and Zn) concentrations were determined in the leaf sample. Because it is screening technique, this method was not so sensitive for the determination of the element concentrations present in trace and in this experiment it was not so appropriate for the leaf samples (Table 8.7.2, Appendix 7). It can be noticed that the element concentrations in soil and leaf obtained by the destructive methods were lower than those measured by the non-destructive methods (Table 8.7.3, Appendix 7). Namely, due to sample digesting (soil by aqua regia and leaves by HNO_3 and H_2O_2), some element fractions associated with silicate could not be digested and dissolved totally. However, the non-destructive (WD-XRF technique; Uniqunat software) were less sensitive for the trace element concentration determination, especially for the leaf samples where many of the PTEs (e.g., As, Be, Bi, Cd, Co, Cr, Mo, Pb, Sb and V) were present in low concentrations (Experiment 2, 3 and 5). Otherwise, the concentrations of the elements obtained with ICP-OES and ICP-MS, and WD-XRF, except Pb and V in the soil and Mg, Mn, Na and Zn in the leaf samples, were significantly correlated (for soil R ranged from 0.40 to 0.99, and for leaf R ranged from 0.40 to 0.85; $p<0.05$) (Tables 7.7.4 and 7.7.5, Appendix 7). Thus, both total and (pseudo)total element concentrations obtained by non-destructive and destructive methods were equally evaluated in order to estimate the magnetic parameters as a proxy for potential magnetic PM pollution in the vineyard ambient.

5.6.2.1 Correlations between magnetic parameter values and element concentrations

The significant ($p<0.01$) correlations between magnetic parameters (SIRM and χ) in the soil samples from both commercial and organic vineyards (R=0.84; R=0.60, respectively) were observed. Thus, it seems that these two magnetic parameters could give similar information about magnetic PM content in the soil. According to the correlation analysis between the magnetic parameters and element concentrations in the soil samples, the significant correlations were obtained between soil SIRM values and

pseudo-total concentrations of As, B, Ca, Cr, Mg, Ni and Sb, as well as total-content of Ca, Cr, Fe, K, Mg, Ni, Rb and Zn (Table 8.7.6, Appendix 7). Moreover, in the commercial vineyard, χ correlated with the same element concentrations with which SIRM values also correlated with (Table 8.7.6, Appendix 7). Thus, both magnetic parameters correlated with Fe, which is significant ferromagnetic, and with other PTEs (Table 8.8.6, Appendix 8) that could be naturally associated with total Fe content in the soil (Kabata-Pendias and Pendias, 2001). Those PTEs in the soil mostly originated from the parent rock (Experiments 3, 5), and some of them e.g., Cr, Ni (Experiments 2 and 3) and Sb (Experiment 4) could originate from the surrounding anthropogenic sources in the commercial vineyard. In addition, in the organic vineyard, the significant positive correlations were observed between the soil SIRM values and Bi, Co, Cu, Fe, K, V and Zn pseudo-total concentrations and also Al, Ba, Cu, Fe, K, Na, Rb, Si, Ti, V, Zn and Zr total concentrations (Table 8.7.6, Appendix 7). The χ values significantly correlated with Be, Bi, Cd, Co, Cu, Fe, K, Li, Mn, P, Pb, S, V and Zn pseudo-total concentrations and also with Al, Ba, Co, Cu, Fe, K, Mn, Ni, P, Rb, S, Si, Ti, V, Zn and Zr total concentrations in the soil from the organic vineyard. Finally, all these significant positive correlations between elements and not high SIRM and χ values implied that the soil from the organic vineyard was not so contaminated by airborne PM and associated PTEs, which mostly have a geogenic origin.

Comparing the soil SIRM and soil χ values with pseudo-total and total PTE concentrations obtained in the samples, it can be assumed that these two soil samples were significantly different (Figure 5.6.4, green point-samples from organic vineyard; red points-samples from the commercial vineyard). According to PCA, it can be seen that almost all the determined elements were grouped in the same quadrant characterised the samples from the commercial vineyard. Thus, higher PTE concentrations in the commercial vineyard influenced higher soil SIRM and soil χ values, probably because in the commercial vineyard the overall PTE concentrations in soil were contributed by both geogenic and anthropogenic sources. Finally, soil SIRM and the soil χ were highly associated with the elements in these samples (Figure 5.6.4). Conversely, only the concentrations of As and Pb grouped in the same quadrant with samples from the organic vineyard (Figure 5.6.4), which was generally less polluted ambient than the commercial, but the concentrations of these two elements were

obtained in higher concentrations in the topsoil from the organic than topsoil from the commercial vineyard. Nevertheless, the As and Pb concentrations were measured in the concentrations lower than MAC and their concentrations were significantly correlated each to other (R=0.64; $p<0.01$). Aside to, the environmental implication indices (BGI, CF and Eri) obtained for the soil from organic vineyard implied low contamination by As and Pb (Tables 7.6.6, 7.6.7 and 7.6.8; Appendix 6), which indicated their predominantly geogenic origin.

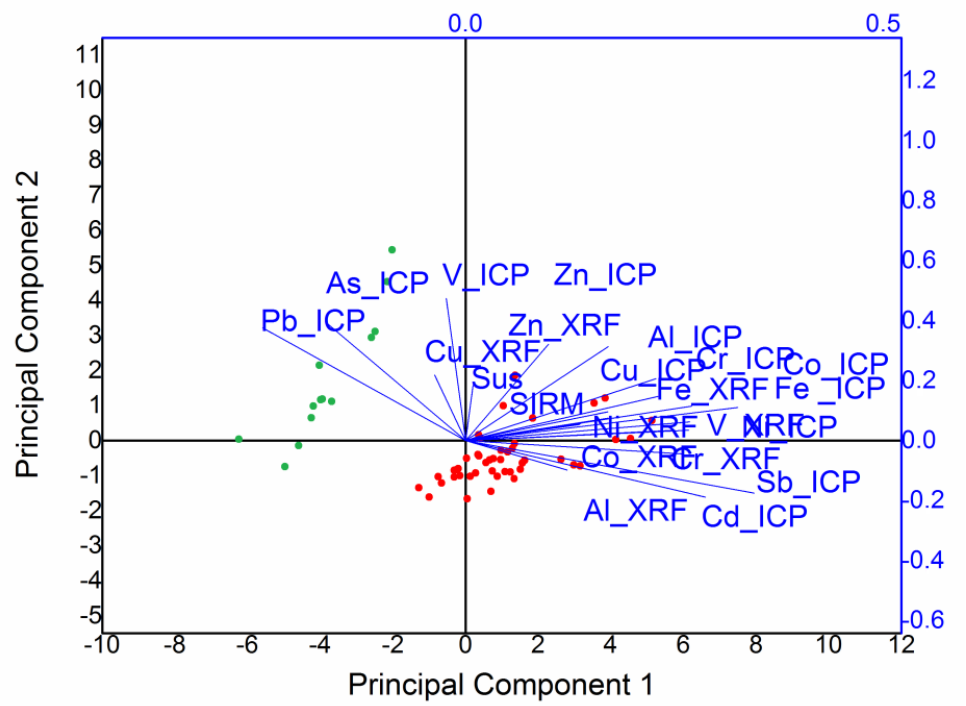


Figure 5.6.4 PCA distinguishing the soil samples from two vineyards (soil samples from organic vineyard are marked green and those from commercial vineyard are marked red) according to the magnetic parameters SIRM and χ (Sus), and element concentrations (total and pseudo-total).

Observing the results for the commercial vineyard, the leaf SIRM and PTEs concentrations, the potential pollution sources were noticed near the particular parcels Thus, because in this study (Experiment 4) the samples were collected from each of the parcels among transect, for each parcel median, maximum and minimum were presented by the box-plots and these box plots were obtained for all phases through the grapevine season. According to these box plots graphs and applied Wilcoxon Signed Rank Test, the significant ($p<0.05$) differences between the element concentrations and SIRM values through the parcels were observed only for Cr, Co and Ni in July and August (Figure 5.6.5a,b,c,d). The most similar spatial patterns for SIRM values and Co,

Cr and Ni concentrations were noticed (Figure 5.6.5a,b,c) in the harvest phase (August). The metal foundry in the vicinity of the vineyard parcel VI (Figure 3.3) possibly influenced the leaf enrichment by the particles with magnetic properties (Figure 5.6.5d) and Co, Cr and Ni concentrations (Figure 5.6.5a,b,c), as well. Usually, areas with long-term industrial emissions of PTEs are expected to be highly contaminated (Massas et al., 2013; Kostarelos et al., 2015).

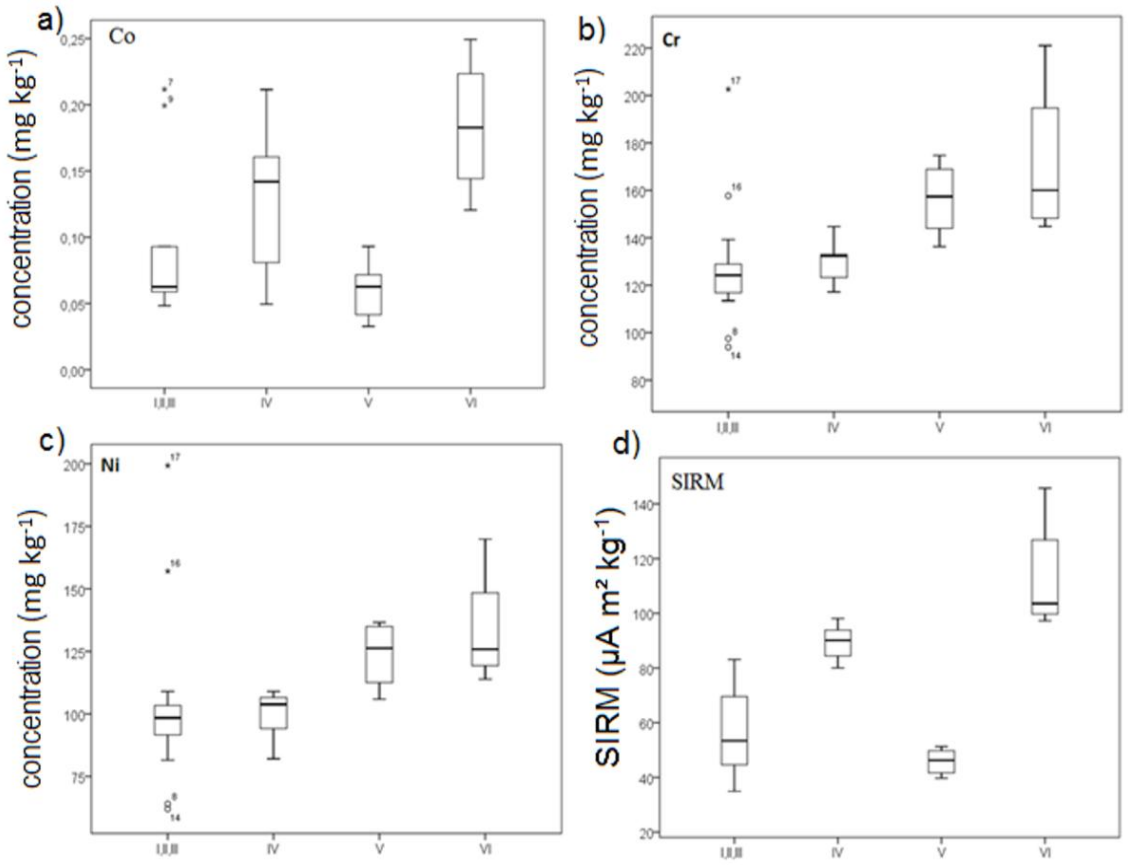


Figure 5.6.5 Spatial distribution of a) Co; b) Cr; c) Ni concentrations (mg kg^{-1}) and d) leaf SIRM values (µA m^2 kg^{-1}) through the parcels in the harvest phase; the middle line of the box represents the median value, top and bottom represent first and third quartiles and whiskers represent maximum and minimum of values; "°" represent outliers and "*" represent extremes (Milićević et al., 2018b).

In the case of both investigated vineyards, the leaf χ values did not distinguish some specific polluted sampling sites and these values only correlate with a few elements. In the commercial vineyard leaf χ values correlated with Cr, Fe and Pb concentrations and in the organic vineyard with Mg and Bi concentrations. Thus, this magnetic parameter even measured in low quantities correlate with Fe which have very strong and positive response to magnetic field (Salo, 2017), and also with Bi which is in soil usually present as chalcopyrite (pyrite), which has ferrimagnetic properties and has

also strong and positive response to magnetic field (Salo, 2017). In addition, the correlation between χ values and Cr concentration could be explained by the association of Cr with Fe which have strong ferromagnetic properties. In the commercial vineyard the leaf SIRM values were significantly ($p<0.01$ and $p<0.05$) correlated with the pseudo-total concentrations of As, Ba, Ca, Co, Cr, Mg, Sb and Sr and total concentrations of Ca, Si, and Sr in the samples (Table 8.7.7, Appendix 7), and with Ba, Bi, Ca, Co, Cr, Fe, Li, Mg, Pb and Sr concentrations (ICP-OES and ICP-MS) in organic vineyard (Table 8.7.7, Appendix 7). The similar SIRM correlations with different element concentrations measured in the leaves were obtained in different studies, e.g., with Fe, Zn, Pb. Mn and Cd (Norouzi et al., 2016) and with Fe, Cr, Ni, Pb and Cu (Yin et al., 2013; Cao et al., 2015; Ma et al., 2015). Moreover, Fe and Mn are the macroelements typically present in different mediums while their correlations with Ni, Cu, Zn, Cr, Cd and Pb are typically related to the road traffic pollution (Hofman et al., 2017). In addition, the other PTEs also can be grouped as traffic-related PM originating from abrasion of tires (Zn, Cd and Cu), brake pads and linings (Sb, Cu, Zn, Fe, Ba and Cr), corrosion (Fe, Cd, Zn, Cu, V and Ni), lubricating oils (V, Cd, Cu, Zn and Mo) or fuel additives (V, Cd, Zn and Pb) (Hofman et al., 2017 and references therein). Additionally, As, Cu, Mn, Ni, Pb, and Zn can originate from the combustion process (Wang et al., 2012; Hofman et al., 2017).

Elements such as Co and Ni have very strong and positive ferromagnetic properties and their response to the magnetic field is very strong (Salo, 2017), which supports the obtained patterns of their similar distribution with SIRM values among the parcels in the commercial vineyard (Figure 5.6.5). In this experiment, the leaf SIRM distinguished different pollution intensities as it was also shown in the previously published studies. In accordance to the correlations between the leaf SIRM values and the PTEs concentrations, e.g., Co, Cr, and Ni, there was obvious indication of the anthropogenic pollution presence (Matzka and Maher, 1999; Muxworthy et al., 2003; Mitchell and Maher, 2009; Hofman et al., 2014; Castanheiro et al., 2016). Similar correlations between the SIRM values and Cr, Co and Ni concentrations in the moss samples were observed by Vuković et al. (2015a) and Salo et al. (2016). In parallel, according to PCA, the significant association between the leaf SIRM and Cr and Co concentrations were found for the samples from the commercial vineyard (Figure 5.6.6).

In addition, in the same quadrant are associated the soil samples collected in July and August (red marked samples) in the commercial vineyard, which proved that in these periods there were higher accumulations of Cr and Co in the leaves and SIRM appears to be a reliable proxy for these elements' accumulation on the leaves (Figure 5.6.6).

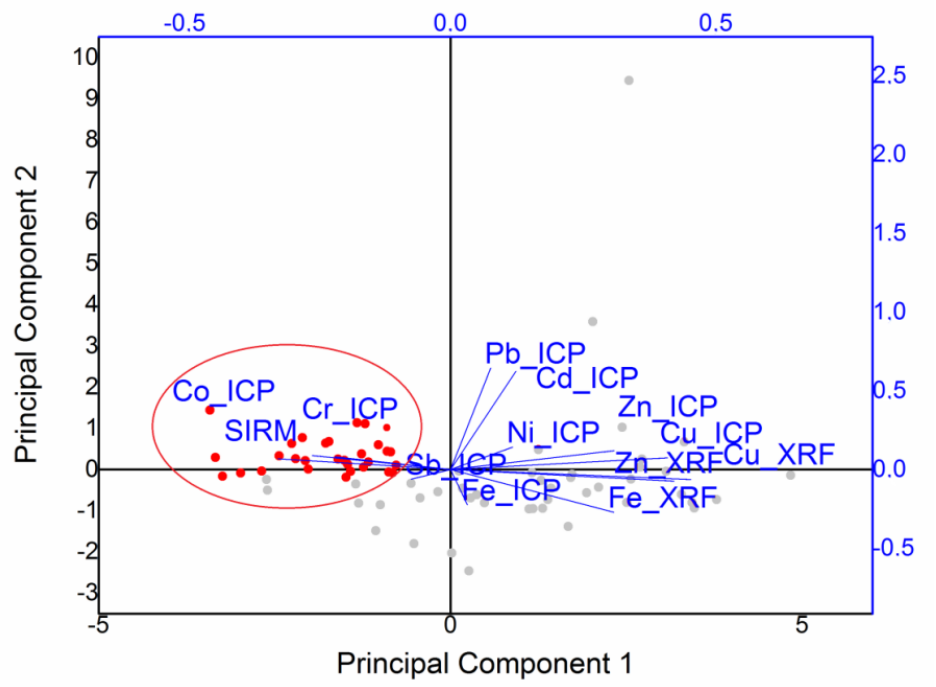


Figure 5.6.6 Association of the leaf SIRM values with Cr and Co concentrations in the commercial vineyard; the samples from July and August are marked with a red circle (red points); grey points represent the samples from the other investigated periods.

In the organic vineyard, the significant correlations were also observed only between the element concentrations and SIRM whereas there were slightly correlations obtained between the leaf χ values and Bi and Mg (Table 8.7.7, Appendix 7), but there were significant correlations between the SIRM and the χ values (R=0.76; $p<0.01$). The significant correlations were observed between leaf SIRM values and Ba, Bi, Ca, Co, Cr, Fe, Li, Mg, Sr. Moreover, the highest correlations were observed for the leaf samples from parcel 5 (Figure 5.6.7, red marked samples). These samples were collected in the organic vineyard through the season from parcel 5 which is located near the Danube River (Figure 3.3). This parcel is not surrounded by the trees and shrubs planted as a barrier for the penetration of possible pollutants from adjacent plots to organic farms.

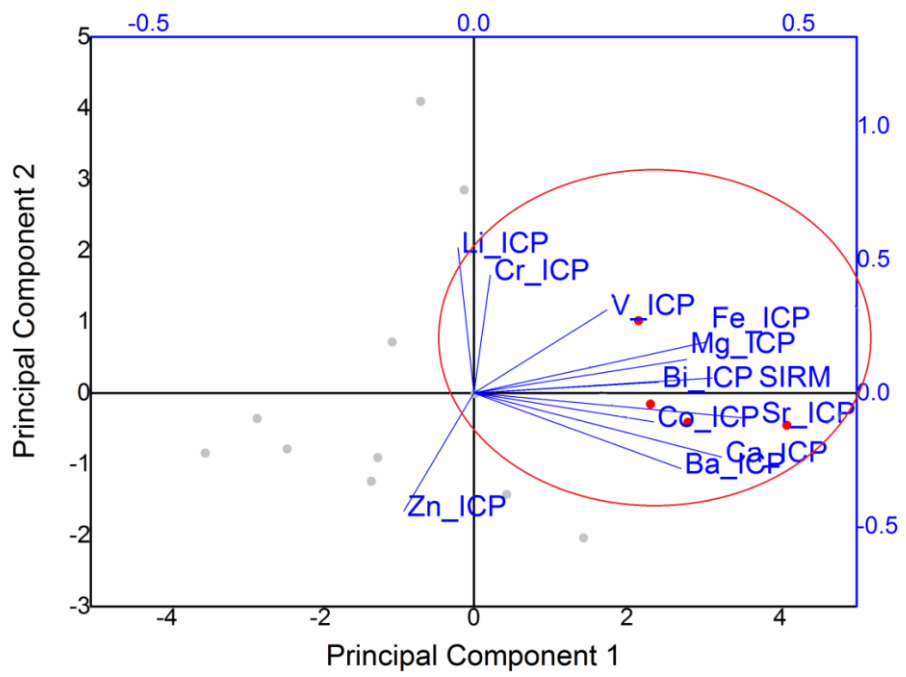


Figure 5.6.7 PCA distinguishing the magnetic PM and PTEs on the leaf (red marked samples represent the samples from parcel 5 and grey samples represent the samples from the other parcels) through the season in the organic vineyard.

According to PCA, in the commercial vineyard the RF values for the PTEs (obtained in Experiments 3 and 5) significantly ($p<0.05$) associated each to other, and in the organic vineyard RFs for Ba, Cu, Mn, Ni and Zn associated in one quadrant also with the leaf SIRM (Figure 5.6.8). Thus, it can be claimed that the higher RFs and SIRM obtained for the leaves from the organic vineyard imply more intensive indication of a neighbor or remote air pollution by magnetic PM and PTEs probably because of the absence of the foliar agrochemical application in the vineyard this RF was higher because the PTEs could not enter through the root system to inner parts of grapevine (Experiment 5).

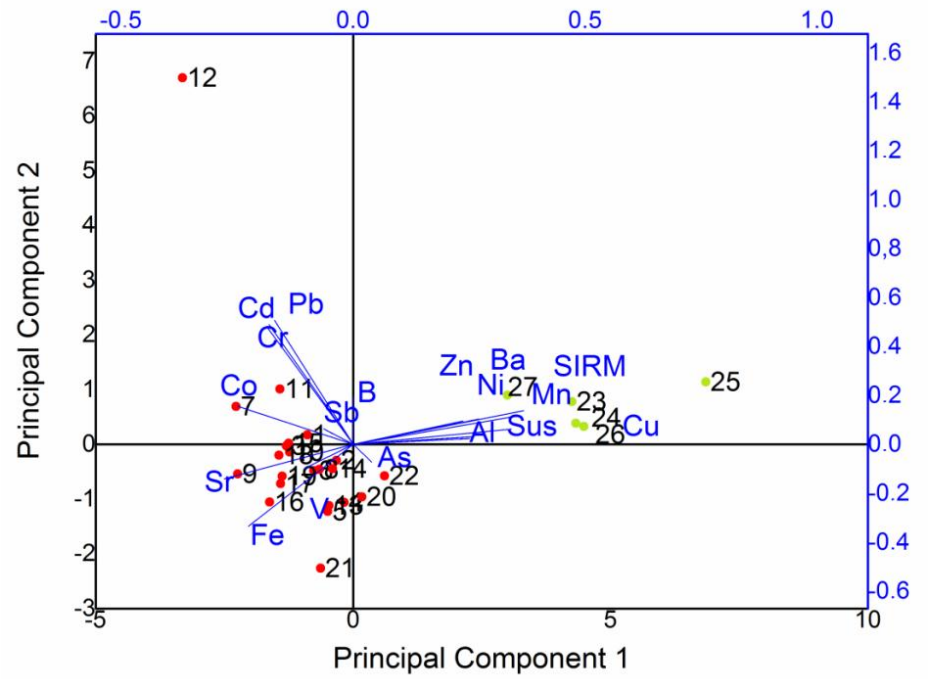


Figure 5.6.8 Ratio Factor (RF) of PTEs (Experiments 2 and 5) comparison with the leaf SIRM obtained for the samples from commercial (red samples 1-22) and organic (green samples 23-27) vineyards.

The grapevine leaves from the investigated vineyards, probably because of the rough structure and plate surface, could keep the deposed particles fixed on their surface and give an indication of atmospheric deposition of magnetic PM and PTEs–Co, Cr and Ni, but also As, Sr, Mn and Zn in the commercial vineyard. Moreover, in the organic vineyard, the grapevine leaves could indicate magnetic PM and Bi, Co, Cr, Fe and Sr originating from the air deposition. Finally, according to the obtained SIRM values and the element concentrations, the grapevine leaves could bioindicate air pollution by magnetic PM and some PTEs in the vineyards.

Finally, according to the results presented in Experiment 6, both magnetic parameters (SIRM and χ) could be indicative for the existence of pollution. These non-destructive techniques could be suitable only as screening methods for the ambient pollution assessment, but more detailed analysis at the recognised hot spots of the pollution would be necessary to be performed. For example, more extensive magnetic measurements in the samples should be done in order to prove these obtained results. For WD-XRF measurements performed on the leaf material, the specific calibration should be done because the used Uniquant program can be only a screening method since it is not so sensitive to detect the PTEs present in traces in the samples.

6 Conclusion

6.1 Conclusion remarks

Through the six experiments performed in the experimental, commercial and organic vineyards, overview of the main conclusions has been given for each experiment. Based on the results from Experiment 1 conducted in the experimental vineyard, the following items can be concluded:

- The highest concentrations of most determined elements in the soil were isolated by the solutions in the following order: aqua-regia < acid solution of CH_3COOH and chelating agent Na_2EDTA < other extractants (deionised H_2O during16 h and 2 h and weak salt solutions $CaCl_2$ NH_4NO_3 and Na_2NO_3).
- Significant correlations were obtained between the concentrations of Cu and S extracted by weak salt solutions ($CaCl_2$ and NH_4NO_3) and deionised H_2O, implying their similar behaviour during extraction or similar origin; Na_2EDTA, CH_3COOH and deionised H_2O 16 h could be appropriate procedures for determining concentrations of Cu and Zn from the soil which probably originated from the same source (agrochemicals). Conversely to extraction procedure using deionised H_2O during 2 h, prolongation of the extraction time to 16 h enabled extraction some of the PTEs (Cu, S and Zn) which were associated each to other, which imply their origin from the same source or could have similar behaviour.
- According to the significant ($p<0.05$) associations, obtained applying the cluster analysis, between the concentrations in the soil extracts and concentrations in the grapevine parts, PTEs (trace elements) bioavailable from soil to the seed and pulp could be extracted by deionised H_2O, while PTEs bioavailable from soil to the grape skin could be extracted by CH_3COOH, Na_2EDTA, $CaCl_2$ and NH_4NO_3; because of the additional air influence on the grapevine leaf surface, single extractions could not give clearly assessment of the trace elements bioavailability from soil to leaves if there are not in parallel estimation of the air deposition influence of the grapevine leaf surface.
- Environmental implication indices (CF, PLI, Igeo and EF) identified pollution among the studied parcels, where moderate (T4 and T5 parcels) to extremely (T6 parcel − near the road) pollution sites were estimated in the experimental vineyard.

- In all studied grapevine varieties and their parts, similar element concentrations were obtained, except in *Prokupac* in which measured higher concentrations in the outer grapevine parts (skin and leaf) imply the influence of air deposition. According to biological accumulation formula (BAC), the leaves of *Riesling rain*, *Riesling italian*, *Cabernet sauvignon* and *Cabernet franc* accumulated Zn from the vineyard soils while the leaf of *Riesling rain*, *Burgundy* and *Riesling italian* leaves accumulated Cu from the soil. The skin of *Prokupac* markedly accumulated Ni from the soil.

Based on the results from Experiments 2 and 3 conducted in the commercial vineyard, the following items can be concluded:

- Through the grapevine season, the soil was moderately contaminated by As, B, Co, Cr, Mn, Ni, Pb, Sb and Sr ($1 \leq CF \leq 3$), while contamination by Cd was high ($6 \leq CF$). Comparing with local background soil sample, some of the PTEs (Cr, As and Ni) in the soil seem to have a geogenic origin, while other could originate from the frequent applications of agrochemicals (B, Cd and Mn) or agricultural machines movement or traffic (Co and Sb). Even the PTE concentrations in soil were high; PTEs in the grapevine and wine samples were below the maximum allowable concentrations (MAC).
- The Cr and Ni concentrations in some of the cultivated parcels, which multiple exceeded their content in the local background soil sample, pointed out anthropogenic sources of the elements (nearby foundry or highway) apart from its geogenic origin in the parent material.
- Six single extraction procedures were studied to determine their efficiency and selectivity for each of the measured elements in the vineyard soil. According to calculated mobility factor (MF%), the most effective extractant for isolating PTE from the soil was Na_2EDTA (specifically for extracting Al, As, Ca, Cd, Co, Cu, Fe, K, Mn, Pb, V, Sr and Zn). The following most efficient solution was CH_3COOH (selective for extracting B, Be, Cr, Li and Ni); further, it was NH_4NO_3 (selective for Ba and Sr), while $CaCl_2$ and deionised H_2O were least aggressive for the elements extraction.
- According to the significant ($p<0.05$) associations between the concentrations in the soil extracts and the grapevine parts, obtained by PCA, the most suitable for assessing bioavailability of PTEs from the soil to the grapevine parts (seed, pulp and

skin) were $CaCl_2$, NH_4NO_3 and Na_2EDTA; CH_3COOH acted aggressively, but it was the least suitable extraction solution for estimating the elements bioavailability in the soil–grapevine system; the deionised H_2O was also a suitable extractant for assessing the bioavailability so it can be recommended as an alternative, cost-effective and ecological-friendly extraction procedure for assessing the bioavailability in the soil-grapevine system.

- Barium appeared as the most bioavailable element originating from the soil; Ni from the soil appeared as bioavailable to the seed, skin and leaf; Cr from the soil was only bioavailable to the seed, probably due to frequent pesticide applications in the seed's development phase; $CaCl_2$ and NH_4NO_3 extracted Mn from the soil, which concentrations were correlated with Mn concentrations measured in the leaf and the skin; in the soil-grapevine leaf system through the grapevine season, Mn, Ni and Sr proved to be the most bioavailable elements; unlike Cd and Co which were not bioavailable to the grapevine leaf. Because of the near-neutral pH and low OM, Cu was not highly bounded in the soil and it could be bioavailable to the leaf (Na_2EDTA) or it could originate in both mediums (soil and leaf) from the agrochemical application of Cu-fungicides; Cd was strongly bound in the soil and was not bioavailable to the grapevine parts.
- According to the obtained significant correlations (bioavailability assessment) accompanied by the environmental implication assessment (by CF and RF), the dominant source of Ba obtained in the inner grapevine parts was the soil, while the dominant source of Mn in outer grapevine parts was air deposition (foliar Mn-pesticide treatments).
- The environmental risk assessment calculations imply moderate pollution by PTEs in the topsoil, except for Cd which pointed out heavy to extreme soil pollution; the most enriched PTE in the topsoil, Cd, contributed to the environmental risk (RI) in the topsoil in veraison and harvest (July and August) phases. Beside high Cd contamination, only medium bioavailability risk (BRAI) was observed in the vineyard soil; the PTEs soluble under the low acid conditions (CH_3COOH) from soil had a higher influence on BRAI; potential and apparent bioavailability risks could be caused by the moderate sorption of Cd in topsoil (BRAI versus BGI).

- Observing the BAC values, in the beginning of the season (May: leaf set phase and June: leaf flowering phase − the phases of the most intensive grapevine growth) higher bioaccumulation than in other investigated phases were observed for Al, Cd, Cu, Fe, Ni and V (May) and B, Cu and Zn (June) concentrations from the soil to the leaves were observed, these elements mostly originate from the application of the agrochemicals (pesticides); In veraison (July) phase As, Co, Cr, Mn, Pb and Sb mostly accumulated in the leaves and these elements mostly originated from the anthropogenic sources; Ba, Ca, Mg and Sr most accumulated in the leaves in the harvest phase probably because of decreasing grapevine agrochemical treatments in this phase; Cu and Na seem to be mostly accumulated in the leaf from the soil. Contrary in the leaves, B, Cd, Sb and Sr originated also from the other sources (resuspension of the polluted soil, agrochemical application or traffic).
- Potential (non-carcinogenic) and carcinogenic risks for field workers, chronically exposed to the vineyard soil were not observed; both investigated grapevine species (*Cabernet sauvignon and Sauvignon blanc*) from the commercial vineyard and wines were safe for consumption (no non-carcinogenic and low carcinogenic risk were observed).

Based on the results from Experiment 4 conducted in the commercial vineyard, the following items can be concluded:

- *S. girgensohnii* and *H. cupressiforme* moss species showed to be appropriate biomonitor species of the airborne PTE pollution in the agricultural area with frequent agrochemical treatments.
- A reliable "signal" of PTEs can be achieved after 2-month of moss bag exposure (it was especially the case for As, Cr, Cu, Ni, Fe and V). The PTE concentrations in mosses were gradually increasing with prolongation of the exposure time (2 months<4 months<6 months). Still, 6-month moss exposure reflected the air pollution through the entire grapevine season.
- In the beginning of the grapevine season (with frequent agrochemical treatments), the highest element enrichment was observed, especially for Cu and Ni, which probably originate from the Cu and Ni-based agrochemicals. Both investigated moss species showed temporal changes of the PTEs trough the season. The calculated RAFs were higher for *S. girgensohnii* than in *H. cupressiforme* (the exceptions were

RAFs for Co, Gd, Lu, Ni, Pb, Sc, Tb, and Yb). Both investigated moss species could be used in the comparable moss bag surveys across vineyards because they gave the similar "signal" to the ambient element content (the correlation coefficients were for Cr: R=0.70; Cu: R=0.56; Sb: R=0.63; and Ti: R=0.76). Both moss species identified additional pollution sources of PTEs.

- Slightly higher concentrations of Cr, Co, Ni and Fe in moss bags exposed in the vineyard were in the parcel (VI) near the metal foundry.
- Along transects in the vineyard parcels, a decrease in Sb concentration was only observed.
- A significant correlation between the moss and leaf concentrations of Co, Cr and Ni suggested that the grapevine leaves also can be a potential bioiomonitor of the ambient pollution in the vineyard.

Based on the results from Experiment 5 conducted in the organic vineyard, the following items can be concluded:

- Among nine tested single extraction procedures, Na_2EDTA and CH_3COOH were promoted as the most effective for assessing the elements mobility (MF%). 0.44 mol L^{-1} CH_3COOH was more effective than 0.11 mol L^{-1} CH_3COOH. For assessing the mobility of the elements $BaCl_2$ were more effective for macro elements and $CaCl_2$, was more effective for the microelements mobility assessment; because Ca from $CaCl_2$ can make interferences in element determination, NO_3^- salts could be more suitable for the mobility assessment; NH_4NO_3 was more suitable than $NaNO_3$ for the elements mobility assessment, because NH_4^+ could bind complexes with PTEs. Deionised H_2O extracted only the soluble elements' quantities (lower MF% than MF% obtained for other extractions) from the soil and prolongation of the extraction time had not proved as more effective for the mobility assessment for this soil type.
- There was not observed soil contamination by PTEs in the organic vineyard, with exception of B in the topsoil samples, especially in July. The low Cd concentration in the soil from organic vineyard was observed, but it seems to be a very mobile element in this soil type and it had a high influence on the environmental (RI) and bioavailability risks (BRAI).
- In organically grown grapes, lower PTE concentrations than in the grapes from experimental and commercial vineyards were obtained.

- According to the calculated BAC, the organically growth grapevine varieties are not hyper-accumulators of PTEs.
- According to the multivariate analysis, B in the parts of the grapevine originated mostly from the air and Cd originated mostly from the soil. Higher concentrations of PTEs were obtained in outer (leaf, petiole and skin) than inner (pulp and seed) grapevine parts, which were also observed by the calculated RF. The leaves in the organic vineyard intensively reflect the air pollutants deposition.
- The air pollution assessed by the moss bag technique in the organic vineyard implied that the organic vineyard ambient was less polluted than the commercial vineyard and urban area (urban background, suburban areas and crossroads); some quantities of B in the mosses which probably originated from the agrochemicals were observed in the organic vineyard in the period of the grapevine growth.
- The organic growth agricultural areas represented a safer working ambient for the field workers and for the growing the grapes than commercial ones.

Based on the results from Experiment 6 performed in order to test whether the non-destructive method could be applicable as cost-effective and easy-applicable for pollution screening in the commercial and the organic vineyards, the following can be concluded:

- Magnetic parameters (SIRM and χ) can represent a reliable proxy for the environmental pollution; there were some differences between the distributions of SIRM and χ through the grapevine season, which were probably influenced by the grain size of magnetic PM.
- More reliable parameter for indicating leaf PM was SIRM; the leaf SIRM could indicate the most polluted hot spots (parcels and periods) in the vineyard ambient recognised previously applying the chemical analyses on the same soil and leaf samples.
- SIRM and χ were correlated each to other, but there were not the correlations between the same parameter obtained for different matrixes (soil and leaf).
- Non-destructive WD-XRF with Uniquant software could be a suitable technique for PTEs screening in the soil and the leaf samples, but for the analysis of some materials such as plant (leaf) with PTEs presented in traces, the specific calibration on more similar material to plant should be done.

- The magnetic parameters in the soil were significantly correlated with those elements, which mostly have a geogenic origin.
- The leaf SIRM could indicate site-specific pollution in the vineyard ambient; the grapevine leaves could be used as potential biomonitors of the ambient pollution and magnetic parameters could represent a proxy for the magnetic PM and some PTE pollution in the vineyard ambients.

6.2 General conclusions

The studies in agricultural areas have been limited only to the investigation of several elements in soil (mostly these prescribed by the regulations − As, B, Cd, Cr, Cu, Pb, Ni and Zn) and plants (fresh vegetables or fruits − As, Cd and Pb) grown on the soil. The use of agrochemicals, which nowadays represent the necessary means for improving plants growth, introduce various additions and impurities (e.g. PTEs, REEs), which can be accumulated in soil and further can be uptake by the plants and accumulated in different plant parts (food crops). Further, the pollutants present in the agricultural environment could have an influence on the field workers' and consumers' health. This doctoral dissertation focused on the above-mentioned issues in a more detailed way than it was done in available scientific literature. The aim of this dissertation was to investigate PTEs in the soil−plant−air system in three specific vineyard ambients by elaborating on: i) the elements mobility and bioavailability using nine single extraction procedures, accompanied with environmental risk and health risk assessment and ii) the grapevine leaves and mosses (*S. girgensohnii* and *H. cupressiforme*) as bioindicators of air pollution by the PTEs. The conclusions from all six experiments could be summarised in the next items:

- The weak acid solution (CH_3COOH) and chelating agent (Na_2EDTA) were proved to be effective for extracting higher percentage (mobility factor − MF%) of the total element content in the soil samples while weak salt solutions ($CaCl_2$, NH_4NO_3 and $NaNO_3$) and deionised H_2O were less effective (lower MF%). Since natural reactions and process in the soil usually are not too aggressive, aggressive solutions were not appropriate to assess PTE bioavailability from soil to plant (aqua regia or CH_3COOH − Experiment 1 and 2). There is not a unique extractant which could uniformly assess the bioavailability of all elements from different soil types, but the chelating agent

and weak salt solutions could be promoted as the most appropriate single extraction procedures for assessing the PTE bioavailability among the tested extractants (Experiments 1, 2, 3 and 5). Deionised H_2O (Experiment 1: Cu, Zn and S; Experiment 2: Ba, Cr, Cu, Sr, Fe, Ni and Experiment 3: Mn) can be recommended also as an appropriate single extraction procedure for bioavailability assessment, but also as a low-cost and eco-friendly extractant.

- Various environmental implication indices differentiated geogenic from the anthropogenic origin of the PTEs in the vineyard and enable a better understanding of mobility and bioavailability of the elements. According to the environmental implication indices, some temporal fluctuations of PTE pollution in the vineyards were revealed (Experiment 3). Various equations for environmental risk assessment showed as appropriate way to calculate dimensionless-unit concentrations, which were more comparable between different ambients (Experiment 5) and which could be used for pointing out the most polluted locations (Experiment 1: parcel near the road; Experiment 2 and 3: parcel near the metal foundry and near the highway road; Experiment 5: parcels more exposed to the atmospheric deposition than other studied parcels).
- Active moss bag technique could be appropriate for assessing air quality in the vineyard ambients. Both studied mosses (*S. girgensohnii* and *H. cupressiforme*) gave a reliable "signal" of PTE enrichment after 2-month exposure period in the vineyard ambient, but with prolongation of the exposure time, the PTE moss enrichment was increasing. The 6-month exposure period should be promoted in comparative studies for observing the air quality through the entire grapevine growing season surely covering all treatments with agrochemicals in different vineyard ambients. Even the grapevine leaves as biomonitors were not such sensitive as mosses, but they could be used to identify hot-spots of pollution.
- According to the obtained PTE concentrations in the soil and grapevine parts, calculated environmental implication indices and PTE enrichment in the moss bags, the organic vineyard could be less polluted grapevine growing ambient than the experimental and the commercial vineyards.
- Magnetic parameters could be a reliable proxy for screening the ambient pollution in the vineyard. Screening, cost-effective and non-destructive techniques such as WD-

XRF with Uniquant software (semi-quantitative) and indicative SIRM and magnetic χ showed as appropriate for detecting the pollution hot spot in the vineyards.

- Finally, the high PTE concentrations in the soil (especially in the commercial vineyard) did not have an adverse impact on the field worker health, and the grapevine and wine prepared from the grapes grown in the vineyards were safe for the consumption. The values for observed health risk for workers and consumers were slightly lower in the organic vineyard, which could indicate that the organic vineyard could be a long-term safer working ambient, and organically grown grapes could be safer for long-term and frequent consumption.

In the end, these results represent the comprehensive assessment of PTE mobility and bioavailability from soil to grapevine, biomonitoring of the air pollution and environmental and health risk assessment contributing a better understanding of the PTE behaviour in the soil−plant−air system. In addition, the results contribute to the improving the moss bag technique which was for the first time conducted in the vineyard ambient.

7 References

Adamo, P., Giordano, S., Vingiani, S., Castaldo, C.R., Violante, P. 2003. Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy). Environ. Pollut. 122, 91–103.

Aiman, U., Mahmood, A., Waheed, S., Malik, R.N. 2016. Enrichment, geo-accumulation and risk surveillance of toxic metals for different environmental compartments from Mehmood Booti dumbing site, Lahore city, Pakistan. Chemosphere. 144, 2229–2237.

Alagić, S., Tošić, S., Dimitrijević, M., Antonijević, M., Njukić, M. 2015. Assessment of the quality of polluted areas based on the content of heavy metals in different organs of the grapevine (*Vitis vinifera*) cv Tamjanika. Environ. Sci. Pollut. R. 22, 7155−7175.

Aničić, M., Tasić, M., Frontasyeva, M.V., Tomašević, M., Rajšić, S., Strelkova, L.P., Popović, A. 2009a. Active biomonitoring with wet and dry moss: A case study in an urban area. Environ. Chem. Lett. 7, 55−60.

Aničić, M., Tasić, M., Frontasyeva, M.V., Tomašević, M., Rajšić, S., Mijić, Z., Popović A. 2009b. Active moss biomonitoring of trace elements with Sphagnum girgensohnii moss bags in relation to atmospheric bulk deposition in Belgrade, Serbia. Environ. Pollut. 157, 673–679.

Aničić, M., Tomašević, M., Tasić, M., Rajšić, S., Popović, A., Frontasyeva, M.V., Lierhagen, S., Steinnes, E. 2009c. Monitoring of trace element atmospheric deposition using dry and wet moss bags: Accumulation capacity versus exposure time. J. Hazard Mater. 171, 182–188.

Aničić Urošević, M., Vuković, G., Tomašević, M., 2017. Biomonitoring of Air Pollution Using Mosses and Lichens, A Passive and Active Approach, State of the Art Research and Perspectives. Nova Science Publishers, New York, USA, ISBN: 978-1-53610-212-3.

Anju, M., Banerjee, D.K. 2011. Associations of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. Environ. Monitor. Assess. 176, 67–85.

Antić-Mladenović, S., Frohne, T., Kresović, M., Stark, H.J., Tomić, Z., Ličina, V., Rinklebe, J. 2017. Biogeochemistry of Ni and Pb in a periodically flooded arable

soil: Fractionation and redox-induced (im)mobilization**,** J. Environ. Manage. 186, 141–150.

Antoniadis, V., Shaheen, S.M., Boersch, J., Frohne, T., Du Laing, G., Rinklebe, J. 2017a. Bioavailability and risk assessment of potentially toxic elements in garden edible vegetables and soils around a highly contaminated former mining area in Germany. J. Environ. Manag. 186, 192–200.

Antoniadis, V., Golia, E.E., Shaheen, S.M., Rinklebe, J. 2017b. Bioavailability and health risk assessment of potentially toxic elements in Thriassio Plain, near Athens, Greece. Environ. Geochem. Health. 39, 319–330.

Antoniadis, V., Levizou, E., Shaheen, S.M., Sik Ok; Y., Sebastian, A., Baum, C., Prasad, M.N.V., Wenzel, W.W., Rinklebe, J. 2017c. Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation–A review. Earth Sci. Rev. 171, 621−645.

Aparecida de Sá, A., Ernani, P. 2016. Boron Leaching Decreases with Increases on Soil pH, Rev. Bras. Cienc. Solo. 40.

Ares, Á., Aboal, J.R., Carballeira, A., Giordano, S., Adamo, P., Fernández, J.A. 2012. Moss bag biomonitoring: A methodological review. Sci. Total Environ. 432, 143–158.

Ares, Á., Aboal, J.R., Carballeira, A., Fernández, J.A. 2015. Do moss bags containing devitalized *Sphagnum denticulatum* reflect heavy metal concentrations in bulk deposition? Ecol. Indic. 50, 90–98.

Asgaria, N., Ayoubia, S., Demattêb, J.A.M. 2018. Soil drainage assessment by magnetic susceptibility measures in western Iran. Geoderma Regional. 13, 35–42.

Baird, C., Cann, M. 2012. Environmental Chemistry. W. H. Freeman and Company, New York, NY 10010.

Bakircioglu, D., Bakircioglu Kurtulus, Y., Ibar H., 2011. Comparison of Extraction Procedures for Assessing Soil Metal Bioavailability of to Wheat Grains, Clean - Soil Air Water. 39, 728 – 734.

Balasooriya, B.L.W.K., Samson, R., Mbikwa, F., Vitharana, W.A.U., Boeckx, P., Van Meirvenne, M. 2009. Biomonitoring of urban habitat quality by anatomical and chemical leaf characteristics. Environmental and Experimental Botany. 65, 386−394.

Barandovski, L., Frontasyeva, M.V., Stafilov, T., Sajn, R., Pavlov, S.S., Enimiteva, V. 2012. Trends of atmospheric deposition of trace elements in Macedonia studied by the moss biomonitoring technique. J. Environ. Sci. Health, Part A Toxic/Hazardous Subst. Environ. Eng. 47, 2000–2015.

Bargagli, R. 1998. Trace Elements in terrestrial Plants: An Ecophysiological Approach to Biomonitoring and Biorecovery. Springer-Verlag, Heidelberg.

Barrow, N.J. 1999, The four laws of soil chemistry: the Leeper lecture 1998. Aust. J. Soil Res. 37, 787–829.

Beckhoff, B., Kanngieber, B., Langhoff, N., Wedell, R., Wolff, H. 2006. Handbook of Practical X-Ray Fluorescence Analysis, Springer, 863.

Beckett, P.H.T. 1989. The use of extractants in studies on trace metals in soils, sewage sludges and sludges-treated soils. Adv. Soil Sci. 9, 144–176.

Berg, T., Steinnes, E. 1997. Use of mosses (Hylocomium splendens and Pleurozium schrebery) as biomonitors of heavy metal deposition: from relative to absolute deposition values. Environ. Pollut. 98, 61–71.

Bilos, C., Colombo, J.C., Skorupka, C.N., Rodriguez Presa, M.J. 2000. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. Environ. Pollut. 111,149-158.

Blundell, A., Dearing, J.A., Boyle, J.F., Hannam, J.A. 2009. Controlling factors for the spatial variability of soil magnetic susceptibility across England and Wales. Earth-Sci. Rev. 95, 158–188.

Bo, V.S. 1986. Verordnung über Schadstoffgehalt im Boden, Swiss Ordinance on Pollution in Soils Nr. 814.12. Publ. Eidg. Drucksachen und Materialzentrale (EDMZ), 3000, Bern.

Bowers, J. E., and Meredith, C. P. 1997. The parentage of a classic wine grape, Cabernet Sauvignon. Nature Genetics, 16, 84–87.

Boyko, T., Scholger, R., Stanjek, H. 2004. Topsoilmagnetic susceptibility mapping as a tool for pollution monitoring: repeatability of in situ measurements. J. Appl. Geophys. 55, 249–259.

Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soils constituents; J. Colloid Interface Sci. 277, 1–18.

Bravo, S., Amorós, J.A., Pérez-de-los-Reyes, C., García, F.J., Moreno, M.M., Sánchez Ormeño, M., Higueras, P. 2017. Influence of the soil pH in the uptake and bioaccumulation of heavy metals (Fe, Zn, Cu, Pb and Mn) and other elements (Ca, K, Al, Sr and Ba) in vine leaves, Castilla-La Mancha (Spain), J. Geochem. Explor. 174, 79–83.

Brown, D.H., Bates, J. W. 1990. Bryophytes and nutrient cycling. Bot. J. Linean .Soc. 104, 129–147.

Brümmer, G.W. 1986. Heavy metal species, mobility and availability in soils; in Bernhard, M., Brinckman, F.E., Sadler, P.J. (Eds). The Importance of Chemical 'Speciation' in Environmental Processes; Springer Verlag, Berlin.

Buccolier, A., Buccolieri, G., Dell'Atti, A., Strisciullo, G., Gagliano-Candela, R. 2010. Monitoring of total and bioavailable heavy metals concentration in agricultural soils, Environ. Monit. Assess. 168, 547 – 560.

Cao, H., Chen, J., Zhang, J., Zhang, H., Qiao, L., Men, Y. 2010. Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. J. Environ. Sci. 22, 1792–1799.

Cao, L., Appel, E., Hu, S., Yin, G., Lin, H., Rösler, W. 2015. Magnetic response to air pollution recorded by soil and dust-loaded leaves in a changing industrial environment. Atmos. Environ. 119, 304–313.

Capozzi, F., Giordano, S., Di Palma, A., Spagnuolo, V., de Nicola, F., Adamo, P. 2016a. Biomonitoring of atmospheric pollution by moss bags: discriminating urban-rural structure in a fragmented landscape. Chemosphere 149, 211–219.

Capozzi, F., Giordano, S., Aboal, R.J., Adamo, P., Bargagli, R., Boquete, T., Di Palma, A., Real, C., Reski, R., Spagnuolo, V., Steinbauer, K., Tretiach, M., Varela, Z., Zechmeister, H., Fernandez, A.J. 2016b. Best options for the exposure of traditional and innovative moss bags: a systematic evaluation in three European countries. Environ. Pollut. 214, 362–373.

Castañeda Miranda, A.G., Chaparro, M.A.E., Chaparro, M.A.E, Böhnel, H.N. 2016. Magnetic properties of *Tillandsia recurvata L.* and its use for biomonitoring a Mexican metropolitan area. Ecol. Indic. 60, 125–136.

Castañeda Miranda, A.G., Böhnel, H., Molina-Garza, R., Chaparro, M.A.E. 2014. Magnetic evaluation of TSP-filters for air quality monitoring. Atmos. Environ. 96, 163–174.

Castanheiro, A., Samson, R., De Wael, K. 2016. Magnetic- and particle-based techniques to investigate metal deposition on urban green. Sci. Total Environ. 571, 594–602.

Chen, H., Teng, Y., Lu, S., Wang, Y., Wang, J. 2015. Contamination features and health risk of soil heavy metals in China. 512−513, 143−153.

Cottenie, A., Verloo, M. 1984. Analytical diagnosis of soil pollution with heavy metals. Fresenius J. Anal. Chem. 317, 389–393.

Culicov, O.A., Yurukova, L. 2006. Comparison of element accumulation of different moss and lichen bags exposed in the city of Sofia (Bulgaria). J. Atmos. Chem. 55, 1–12.

Dangić, A., Dangić, J. 2007. Arsenic in the soil environment of central Balkan Peninsula, southeastern Europe: occurrence, geochemistry, and impact. In: Bhattacharya, P., Mukherjee, B.B.A., Bundschuh, J., Zevenhoven, R., Loeppert, H.R. (Eds.), Arsenic in Soil and Groundwater Environment, Trace Metals and other Contaminants in the Environments. 9. 207–236.

Dekkers, M.J. 1997. Environmental magnetism. Geologie en Mijnbouw 76, 163–182.

Deljanin, I., Antanasijević, D., Vuković, G., AničićUrošević, M., Tomašević, M., Perić-Grujić, A., Ristić, M. 2015. Lead spatio-temporal pattern identification in urban microenvironments using moss bags and the Kohonen self-organizing maps. Atmos. Environ. 117, 180–186.

Desenfant, F., Petrovský, E., Rochette, P. 2004. Magnetic signature of industrial pollution of stream sediments and correlation with heavy metals: case study from South France. Water Air Soil Pollut. 152, 297–312.

Devesa-Rey, R., Barral, M.T., Jouanneau, J.-M., Diaz Fierros, F. 2010. Analysis of the degree of contamination and evolution in the last 100 years of the composition of the bed sediments of the Anllons Basin. Environ. Earth Sci. 61, 1401–1417.

Di Palma, A., Crespo Pardo, D., Spagnuolo, V., Adamo, P., Bargagli, R., Cafasso, D., Capozzi, F., Aboal, J.R., González, A.G., Pokrovsky, O., Beike, A.K., Reski, R., Tretiach, M., Varela, Z., Giordano, S., 2016. Molecular and chemical

characterization of a *Sphagnum palustre* clone: Key steps towards a standardized and sustainable moss bag technique, Ecol. Indic. 71, 388–397.

DIN, Deutsches Institut für Normung, Bodenuntersuchungs. 1995. Extraktion von Spurenelemente mit Ammonium-nitralüsung. Vornorm DINV 19730; DIN Boden-Chemische Bodenuntersuchungs – verfahren, Berlin.

Directive (92/43/EEC) of Environmental European Commission of the council of 21 May 1992 relating to Habitats. Off. J. Eur. Commiss. NoL206/50 (22.07.92).

Dołęgowska, S., Migaszewski, Z. M. 2013. Anomalous concentrations of rare earth elements in the moss–soil system from south-Central Poland. Environ. Pollut. 178, 33–40.

Duodu, G.O., Goonetilleke, A., Ayoko, G.A. 2016. Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. Environ. Pollut. 219, 1077–1091.

Duplay, J., Semhi, K., Errais, E., Imfeld, G., Babcsanyi, I., Perrone, T. 2014. Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France): The impact of cultural practices. Geoderma, 230–231, 318–328.

EEA (European Environmental Agency), 2016. Page Last modified 02 Dec 2016. Accessed 30.08.2018.

EEA (European Environmental Agency), 2007. Diffuse sources. Accessed 30.08.2018.

Ettler, V. 2016. Soil contamination near non-ferrous metal smelters: A review. Appl. Geochem. 64, 56–74.

EU Council Directive 86/278/EEC.on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Off. J. Eur. Union 181, 6–12.

European Commission, 2012. Commision implementing regulation (EU) No. 203/2012; eur-lex.europa.eu, Accessed: 21.08.2018.

EU Rules for Organic Wine Production, Background, evaluation and further sector development. 2012. Ifoam EU Group, European Commission, Brussels, Belgium.

Evans, L.J. 1989. Chemistry of metal retention by soils. Environ. Sci. Technol. 23, 1046–1056.

Evans, E., Heller, P. 2003. Environmental Magnetism: Principles and Applications of Enviromagnetics. Elsevier, ISBN 0080505783.

Fernández, J.A, Ares, A., Rey-Asensio, A., Carballeira, A., Aboal, J.R. 2010. Effect of growth on active biomonitoring with terrestrial mosses. J. Atmos. Chem. 63, 1−11.

Fetter, C. 1993. Contaminant Hydrogeology. Macmillan, New York.

Finnish Standards Association 1994. Air protection. Bioindication. Moss bag method. SFS 5794. Finnish Standards Association, Helsinki (in Finnish)

Flanders, P. J. 1994. Collection, measurement, and analysis of airborne magnetic particulates from pollution in the environment (invited). J. Appl. Phys. 75, 5931

Flores-Vélez, L.M, Ducaroir, J., Jaunet, A.M., Robert, M. 1996. Study of the distribution of copper in an acid sandy vineyard soil by three different methods. Eur. J. Soil Sci. 47,523–532.

Food and Agriculture Organization of the United Nations. 1998. World reference base for soil resources. International Society of Soil Science, ISBN 92-5-104141-5.

Gautam, P., Blaha, U., Appel, E. 2005. Magnetic susceptibility and dust loaded leaves as a proxy of traffic-related heavy metal pollution in Kathmandu city, Nepal. Atmos. Environ. 39, 2201–2211.

Ghasemi, S., Siavash Moghaddam, S., Rahim, A., Damalas, C.A., Naji, A. 2018. Ecological risk assessment of coastal ecosystems: The case of mangrove forests in Hormozgan Province, Iran. Chemosphere. 191, 417–426.

Gimeno-García, E., Andreu, V., Boluda, R. 1996. Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soils. Environ. Pollut. 92, 19–25.

Goldberg, S., Lesch, S.M., Suarez, D.L. 2000. Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model. Soil Sci. Soc. Am. J. 64, 1356–1363.

González, G.A., Pokrovsky, S.O. 2014. Metal adsorption on mosses: Toward a universal adsorption model. J. Colloid Interface Sci. 415, 169–178.

Goodman, T.G., Roberts, M.T. 1971. Plants and soils as indicators of metals in the air. Nature 231, 287–292

Grantz, D.A., Garner, J.H.B., Johnson, W.D. 2003. Ecological effects of particulate matter. Environ. Int. 29, 213–39.

Grigoratos, T., Martini G. 2015. Brake wear particle emissions: A review. Environ. Sci. Pollut. Res. 22, 2491–2504.

Guerreiro, C., Gonzalez Ortiz, A., de Leeuw, F., Viana, M., Horalek, J. 2016. Air quality in Europe. European Environment Agency, ISBN 978-92-9213-847-9.

Guo, W., Liu, X., Liu, Z., Li, G. 2010. Pollution and Potential Ecological Risk Evaluation of Heavy Metals in the Sediments around Dongjiang Harbor, Tianjin. Procedia. Environ. Sci. 2, 729–736.

Guo,W., Nazimc, H., Lianga, Z., Yanga, D. 2016. Magnesium deficiency in plants: An urgent problem. Crop J. 4, 83–91.

Gupta, S.K., Vollmer, M.K., Krebs, R. 1996. The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. Sci. Total Environ. 178, 11–20.

Hakason, L. 1980. An ecological risk index for aquatic pollution control, a sedimentological approach. J. Water Research. 14, 975–1001.

Hall, J.L. 2002. Cellular mechanisms for heavy metal detoxification and tolerance. J. Exp. Bot., 53, 1−11.

Hanesch, M., Rantitsch, G., Hemetsberger, S., Scholger, R. 2007. Lithological and pedological influences on the magnetic susceptibility of soil: their consideration in magnetic pollution mapping. Sci. Total Environ. 382, 351–363.

Hannam, J.A., Dearing, J.A., 2008. Mapping soil magnetic properties in Bosnia and Herzegovina for landmine clearance operations. Earth Planet. Sci. Lett. 274, 285–294. Hansard, R., Maher, B.A., Kinnersley, R.P., 2012. Rapid magnetic biomonitoring and differentiation of atmospheric particulate pollutants at the roadside and around two major industrial sites in the U.K. Environ. Sci. Technol. 46, 4403–4410.

Hansard, R., Maher, B.A., Kinnersley, R., 2011. Biomagnetic monitoring of industry-derived particulate pollution. Environ. Pollut. 159, 1673−1681.

Hanesch, M.; Scholger, R.; Rey, D. 2003. Mapping dust distribution around an industrial site by measuring magnetic parameters of tree leaves. Atmos. Environ. 37, 5125–5133

Häring, A., Dabbert S., Offermann F., Nieberg H. 2001. *Benefits of organic farming forsociety*, European conference – Organic food and farming, Copenhagen, Denmark, 1−8.

Harmens, H., Norris, A.D., Koerber, R.G., Buse, A., Steinnes, E., Ruhling, A. 2008. Temporal trends (1990-2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environ. Pollut. 151, 368-376.

Harmens, H. et al. 2010. Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe. Environ. Pollut. 158, 3144–3156.

Harrison, R.M., Yin, J. 2000. Particulate matter in the atmosphere: which particle properties are important for its effect on health? Sci. Total Environ. 249, 85−101.

Herceg Romanić, S., Vuković, G., Klinčić, D., Atanasijević, D. 2018a. Self-organizing maps for indications of airborne polychlorinated biphenyl (PCBs) and organochlorine pesticide (OCPs) dependence on spatial and meteorological parameters. Sci. Total Environ. 178, 127–132.

Herceg Romanić, S., Vuković, G., Klinčić, D., Matek Sarić, M., Župan, I., Atanasijević, D., Popović, A. 2018b. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Cyprinidae fish: Towards hints of their arrangements using advanced classification methods. Environ. Res. 628–629, 198–205.

Hildebrandt, A., Guillamón, M., Lacorte, S., Tauler, R., Barceló, D. 2008. Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). Water Res. 42,15–26.

Hooda, P. 2010. Trace elements in soil. A John Wiley and Sons, Ltd., Publication, United Kingdom.

Hooda, P. 2010. Assessing Bioavailability of Soil Trace Elements. In: Hooda (Ed.) Trace elements in soil. A John Wiley and Sons, Ltd., Publication, United Kingdom.

Hoodaji, M., Ataabadi, M., Payam Najafi, P. 2012. Biomonitoring of Airborne Heavy Metal Contamination, Air Pollution - Monitoring, Modelling, Health and Control, Mukesh Khare (Ed.) ISBN: 978-953-51-0381-3.

Hofman, J., Wuyts, K., Van Wittenberghe, S., Samson, R. 2014. On the temporal variation of leaf magnetic parameters: seasonal accumulation of leaf-deposited

and leaf-encapsulated particles of a roadside tree crown. Sci. Total Environ. 493, 766–772.

Hofman, J., Maher, B.A., Muxworthy, A.R., Wuyts, K., Castanheiro, A., Samson, R. 2017. Biomagnetic monitoring of atmospheric pollution: a review of magnetic signatures from biological sensors. Environ. Sci. Technol. 51, 6648–6664.

Houba, V.J.G, Lexmond, T.M., Novozamsky, I., vander Lee, J.J. 1996. State of the art and future developments in soil analysis for bioavailability assessment; Sci. Total Environ. 178, 21–28.

Houba, V.J.G., Temmingoff, E.J.M., Gaikhorst, G.A., Van Vark, W. 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. Commun. Soil Sci. Plant Anal. 31, 1299–1396.

Hu, Z.Y., Zhao, F.J., McGrath, S.P. 2005. Sulphur fractionation in calcareous soils and bioavailability to plants, Plant Soil 268, 103 – 109.

Hu, Z., Haneklaus, S., Sparovek, G., Schnug, E. 2006. Rare earth elements in soils. Commun. Soil Sci. Plant Anal. 37, 1381–1420.

Hu, S.Y., Duan, X.M., Shen, M.J., Blaha, U., Roesler, W., Yan, H.T. 2008. Magnetic response to atmospheric heavy metal pollution recorded by dust-loaded leaves in Shougang industrial area, western Beijing. Chin. Sci. Bull. 53, 1555–1564.

Hui-na, Z., Xing-zhong, Y., Guang-ming, Z., Min, J. Jie1, L., Chang, Z., Juan, Y., Hua-jun, H., Zhi-feng, L., Hong-wei, J. 2012. Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. Chemosphere 22, 1470–1477.

Hunt, A., Jones, J., Oldfield, F. 1984. Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. Sci. Total Environ. 33, 129–139.

Inczédy, J. 1976. Analytical Applications of Complex Equilibria, Elliis Horwood, Chichester, England.

Instructions for soil sampling, protocol reported by the Institute of Field and Vegetable Crops, Novi Sad, Serbia, Laboratory of soil and agroecology, http://www.nsseme.com/en/, Accessed 27.12.2017.

International Regulation (EEC) No 2092/91.

Islam, S., Ahmed, K., Al-Mamun, H. 2015. Distribution of trace elements in different soils and risk assessment: A case study for the urbanized area in Bangladesh. J. Geochem. Explor. 158, 212–222.

ISO 11260, 1994. Soil quality: Determination of effective cation exchange capacity and base saturation level using barium chloride solution. International Organisation for Standardisation.

Ivanišević, D., Jakšić, D., Korać, N. in Serbian: Vinogradarski atlas Srbije. 2015. Republički zavod za statistiku Republike Srbije, ISBN- 979-86-6161-138-4.

Jacobson, A.R., Dousset, S., Guichard, N., Baveye, P.C., Andreux, F. 2005. Diuron mobility through vineyard soils contaminated with copper. Environ. Pollut. 138, 250.

Jakovljević, M., Kostić, N., Stevanović, D., Blagojević, S., Wilson, M.J., Martinović, Lj. 1997. Factors influencing the distribution of heavy metals in the alluvial soils of the Velika Morava River Valley, Serbia. Appl. Geochem. 12, 637–642.

Jamshidi-Zanjani, A., Saeedi, M., Li, LY. 2015. A risk assessment index for bioavailability of metals in sediments: Anzali international wetland case study. Environ. Earth. Sci. 73, 2115–2126.

Jiao, W., Chen, W., Chang, A.C., Page, A.L. 2012. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: a review. Environ. Pollut. 168, 44–53.

Jordanova, N., Jordanova, D., Petrov, P. 2016. Soil magnetic properties in Bulgaria at a national scale—challenges and benefits. Glob. Planet. Chang. 137, 107–122.

Juneja, S., Prakash, S. 2005. The chemical form of trivalent chromium in xylem sap of maize (Zea mays L.). Chem. Spec. Bioavailab. 17, 161–169.Kabata–Pendias, A., Mukherjee, A. 2007. Trace elements from soil to human. Springer-Verlag Berlin Heidelberg, Germany.

Kabata-Pendias, A., Mukherjee, A. 2007. Trace Elements From Soil to Human. Springer- Verlag, Berlin Heidelberg, Germany.

Kabata-Pendias, A., Kabata, H. 2001. Trace elements in Soils and Plants, CRC Press, Taylor and Francis Group, LLC, USA.

Kampa, M., Castanas, E. 2008. Human health effects of air pollution. Environ. Poll. 151, 362−367.

Kardel, F., Wuyts, K., Maher, B.A., Hansard, R., Samson, R. 2011. Leaf saturation isothermal remanent magnetization (SIRM) as a proxy for particulate matter monitoring: Inter-species differences and in-season variation. Atm. Environ. 45, 5164−5171.

Kardel, F., Wuyts, K., Maher, B.A., Samson, R. 2012. Intra-urban spatial variation of magnetic particles: Monitoring via leaf saturation isothermal remanent magnetisation (SIRM). Atmos. Environ.

Karimi, R., Ayoubi, S., Jalalian, A., Sheikh-Hosseini, A.R., Afyuni, M. 2011. Relationships between magnetic susceptibility and heavy metals in urban topsoils in the arid and semi-arid region of Isfahan, central Iran. J. Appl. Geophys. 74, 1–7.

Katana, C., Jane, M., Huran, M. 2013. Speciation of Chromium and Nickel in Open-Air Automobile Mechanic Workshop Soils in Ngara, Nairobi, Kenya. World Environ. 3, 143–154.

Kelepertzis, E. 2014. Accumulation of heavy metals in agricultural soils of Mediterranean: Insights from Argolida basin, Peloponnese, Greece. Geoderma. 221−222, 82−90.

Kelepertzis, E., Paraskevopoulou, V., Argyraki, A., Fligos, G., Chalkiadaki, O. 2015. Evaluation of single extraction procedures for the assessment of heavy metal extractability in citrus agricultural soil of a typical Mediterranean environment (Argolida, Greece), J. Soils Sediments 15, 2265−2275.

Kelly, F.J., Fussell, J.C. 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. 60, 504–526

Khan, M.A., Ding, X., Khan, S., Brusseau, M.L., Khan, A., Nawab, J. 2018. The influence of various organic amendments on the bioavailability and plant uptake of cadmium present in mine-degraded soil. Sci. Total Environ. 63, 810–817.

Kim, R. Y., Yoon, J. K., Kim, T. S., Yang, J. E., Owens, G., Kim, K. R. 2015. Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. Environ. Geochem. Health. 37, 1041–1061.

Knox, E.G. 2006. Roads, railways, and childhood cancers. J. Epidemiol. Community Heal. 60, 136–141.

Knutsen, S., Shavlik, D., Chen, L.H., William Lawrence Beeson, M.G., Petersen, F. 2004. The association between particulate air pollution levels and risk of cardiopulmonary and allcause mortality during 22 years follow-up of a non-smoking cohort. Results from the AHSMOG study 15, 44–52.

Kohonen, T. 1982. Self-organized formation of topologically correct feature maps. Biol. Cybern. 43, 59–69.

Kohonen, T. 1991. Self-organizing maps: optimization approaches. In: Kohonen, T., Mäkisara, K., Simula, O., Kangas, J. (Eds.), Artificial Neural Networks, North-Holland, Amsterdam, Netherlands, pp. 981–990.

Kohonen, T. 2013. Essentials of the self-organizing map. Neural Netw. 37, 52–65.

Komárek, M., Čadková, E., Chrastný, V., Bordas, F., Bollinger, J. 2010. Contamination of vineyard soils with fungicides: A review of environmental and toxicological aspects. Environ. Int. 36, 138–151.

Kostarelos, K., Gavriel, I., Stylianou, M., Zissimos, A.M., Morisseau, E., Dermatas, D. 2015. Legacy soil contamination at abandoned mine sites: Making a case for guidance on soil protection. Bull. Environ. Contam. Toxicol. 94, 269-274.

Kravchenko, J., Darrah, T.H., Miller, R.K., Lyerly, H.K., Vengosh, A. 2014. A review of the health impacts of barium from natural and anthropogenic exposure. Environ. Geochem. Health. 36, 797–814.

Kuklinska, K., Wolska, L., Namiesnik, J. 2015. Air quality policy in the U.S. and the EU – a review. Atmos. Pollut. Res. 6, 129−137;

Kupiainen, K. 2007. Road sust from pavement wear and traction sanding. Monograph of Boreal Environ. Res. 20, Helsinki.

Larsson, M., Baken, S., Petter Gustafsson, J., Hadualhejazi, G., Smolders, E. 2013. Vanadium bioavailability and toxicity to soil microorganisms and plants. Environ. Toxicol. Chem. 10, 2266–2273.

Laurie, V.P., Villagra, E., Tapia, J., Sarkis, J.E.S., Hortellani, M.A. 2010. Analysis of major metallic elements in Chilean wines by atomic absorption spectroscopy. Cien. Inv. Agr. 37, 77–85.

Laveuf, C., Cornu, S. 2009. A review on the potentiality of Rare Earth Elements to trace pedogenetic processes. Geoderma 154, 1–12.

Lee, P.-K., Touray, J.-C., Baillif, P., Ildefonse, J.-P. 1997. Heavy metal contamination of settling particles in a retention pond along the A-71 motorway in Sologne, France. Sci. Total Environ. 201, 1–15.

Lehndorff, E., Urbat, M., Schwark, L. 2006. Accumulation histories of magnetic particles on pine needles as function of air quality. Atmos. Environ. 40, 7082–7096.

Li, P., Lin, L., Cheng; H.,i Duan, X., Lei, K. 2015. Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. Ecotoxicol. Environ. Saf. 113, 391−399.

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.

Lin, H., Sun, T., Xue, S., Jiang, X. 2016. Heavy metal spatial variation, bioaccumulation and risk assessment of *Zostera japonica* habitat in the Yellow River Estuary, China. Sci. Total Environ. 541, 435–443.

Liu, X., Lu, R., Lü, Z., Du, J., Jia, F., Li, T., Chen, L., Wu, Y. 2017. Magnetic susceptibility of surface soils in the Mu Us Desert and its environmental significance. Aeolian. Res. 25, 127–134.

Ličina, V., Fotirić Akšić, M., Tomić, Z., Trajković I., Antić Mladenović, S., Marjanović, M., Rinklebe, J. 2017. Bioassessment of heavy metals in the surface soil layer of an opencast mine aimed for its rehabilitation. J. Environ. Manage. 186, 240–252.

Loell, M., Reiher, W., Felix-Henningsen, P. 2011. Contents and bioavailability of rare earth elements in agricultural soils in Hesse (Germany). Z. Pflanzenernähr. Bodenk. 174, 644–654.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder. F.D. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environm. Mgmt. 19, 81–97

Łukasik, A., Magiera, T., Lasota, J., Błonska, E. 2016. Background value of magnetic susceptibility in forest topsoil: assessment on the basis of studies conducted in forest preserves of Poland. Geoderma 264, 140–149.

Ma, M., Hu, S., Cao, L., Appel, E., Wang, L. 2015. Atmospheric pollution history at Linfen (China) uncovered by magnetic and chemical parameters of sediments from a water reservoir. Environ. Pollut. 204, 161–172.

Massas, I., Kalivas, D., Ehaliotis, C., Gasparatos, D. 2013. Total and available heavy metal concentrations in soils of the Thriassio plain (Greece) and assessment of soil pollution indexes. Environ. Monit. Assess. 185, 6751-6766.

Madrid, F., Diaz-Barrientos, E., Madrid, L. 2008. Availability and bioaccessibility of metals in the clay fraction of urban soils of Sevilla. Environ. Pollut. 156, 605–610.

Maher, B. A.; Moore, C.; Matzka, J. 2008. Spatial variation in vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves. Atmos. Environ. 42, 364–373

Manahan, S. 2013. Fundamentals of Environmental and Toxicological Chemistry. CRC Press, New York, ISBN: 978-1-4665-5317-0.

Marcazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R. 2001. Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan (Italy). Atmos. Environ. 35, 4639−4650.

Mari, M., Nadal, M., Schuhmacher, M., Domingo, J.L. 2010. Application of self-organizing maps for PCDD/F pattern recognition of environmental and biological samples to evaluate the impact of a hazardous waste incinerator. Environ. Sci. Technol. 44: 3162–3168.

Markert, B. 1995. Sampling and Sample Pretreatment, In: Quality Assurance in Environmental Monitoring, Quevauviller PH (Ed.) Weinheim: VCH, New York, 215-254.

Markert B.S., Breure A.M., Zechmeister H.G. 2003. Definitions, strategies and principles for bioindications/biomonitoring of the environment. In: Markert, B.A., Breure, A.M., Zechmeister, H.G., (Eds.) Bioindicators/biomonitors. Elsevier, Amsterdam, 3–41.

Markert, B. 2007. Definitions and principles for bioindication and biomonitoring of trace metals in the environment. J. Trace Elem. in Med. Bio. 21, 77–82.

Marschner, H. 2012. Marschner's Mineral Nutrition of Higher Plants, 3rd Edn. London: Academic Press.

Matong, J. M., Nyaba, L., Nomngongo, P. N. 2016. Fractionation of trace elements in agricultural soils using ultrasound assisted sequential extraction prior to inductively coupled plasma mass spectrometric determination, Chemosphere. 154, 249–257.

Matzka, J., Maher, B.A. 1999. Magnetic biomonitoring of roadside tree leaves: Identification of spatial and temporal variations in vehicle-derived particulates. Atmos. Environ. 33, 4565–4569.

Mazurek, R., Kowalska, J., Gąsiorek, M., Zadrożny, P., Józefowska, A., Zaleski, T., Kępka, W., Tymczuk, M., Orłowska, K. 2017. Assessment of heavy metals contamination in surface layers of Roztocze National Park forest soils (SE Poland) by indices of pollution. Chemosphere. 168, 839–850.

Magiera, T., Gołuchowska, B., Jabłońska, M. 2013. Technogenicmagnetic particles in alkaline dusts from power and cement plants. Water Air Soil Pollut. 224, 1389.

McGrath, D. 1996. Application of single and sequential extraction procedures to polluted and unpolluted soils, Sci. Total Environ. 178, 37–44.

Meers, E., Samson, R., Tack, F.M.G., Ruttens, A., Vandegehuchte, M., Vangronsveld, J., Verloo M.G. 2007. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by *Phaseolus vulgaris*. Environ. Exp. Bot. 60, 385–396.

Meeus, C., Eduljee, G., Hutton, M., 2002. Assessment and management of risks arising from exposure to Cd in fertilisers. I. Sci. Total Environ. 291, 167–187.

Michael, E., Friedrich, H. 2003. Environmental magnetism: Principles and applications of enviromagnettics. Elsevier Science, USA. ISBN 0-12-243851-5.

Mihajlovic, J., Rinklebe, J. 2018. Rare earth elements in German soils - A review. Chemosphere 205, 514-523.

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

Milićević, T., Aničić Urošević, M., Vuković, G., Škrivanj, S., Relić, D., Frontasyeva, M.V., Popović, A. 2017b. Assessment of species-specific and temporal variations of major, trace and rare earth elements in vineyard ambient using moss bags. Ecotoxicol. Environ. Saf. 144, 208–215.

Milićević, T., Aničić Urošević, M., Relić, D., Vuković, G., Škrivanj, S., Popović, A. 2018a. Bioavailability of PTE in soil-grapevine (leaf, skin, pulp and seed) system and environmental and health risk assessment, Sci. Total Environ. 626, 528–545.

Milićević, T., Relić, D., Aničić Urošević, M., Vuković, G., Škrivanj, S., Samson, R., Popović, A. 2018b. Integrated approach to environmental pollution investigation – spatial and temporal patterns of potentially toxic elements and magnetic particles in vineyard through the entire grapevine season. Ecotoxicol. Environ. Saf. 163, 245–254.

Minolfi, G., Albanese, S., Lima, A., Tarvainen, T., Fortelli, A., De Vivo, B. 2018. A regional approach to the environmental risk assessment - Human health risk assessment case study in the Campania region. J. Geochem. Explor. 207, 159−168.

Mishra, S.K., Tripathi, S.N. 2008. Modelling optical properties of mineral dust over the Indian Desert. J Geophys. Res. Atmos. 113, 1–19.

Mitchell, R.; Maher, B. A. 2009. Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution. Atmos Environ. 43, 2095–2103.

Mitchell, R., Maher, B.A., Kinnersley, R. 2010. Rates of particulate pollution deposition onto leaf surfaces: Temporal and inter-species magnetic analyses. Environ. Pollut. 158, 1472– 1478.

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.

Moreno, E., Sagnotti, L., Dinarès-Turell, J., Winkler, A., Cascella, A. 2003. Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves. Atmos. Environ. 37, 2967–2977.

Muralikrishna, I.V., Manickam, V. 2017 Environmental Management: Science and Engineering for Industry. Elsevier, ISBN 978-0-12-811989-1.

Muxworthy, A.R., Matzka, J., Davila, A.F., Petersen, N. 2003. Muxworthy, A.R., Matzka , M., Davila , AF., Petersen , N., Magnetic signature of daily sampled urban atmospheric particles, Atmos. Environ. 37, 4163–4169.

Nel, A. 2005. Atmosphere. Air pollution-related illness: effects of particles. Science. 308, 804−806.

Nicholson, K.W., Branson, J.R. 1990. Factors affecting resuspension by road traffic. Sci. Total. Environ. 93, 349–358.

Niesiobędzka, K., 2016. Mobile forms and migration ability of Cu, Pb and Zn in forestry system in Poland, Environ. Earth Sci. 75, 122.

Ninkov, J., Vasin, J., Milić, S., Marinković, J., Sekulić, P., Hansman, Š., Živanov, M. 2014. in Serbian. Karakterizacija zemljišta vinograda za oznaku geografskog porekla vina−pilot projekat−Šumadijski vinogradarski rejon. Matica Srpska Library, Novi Sad, Serbia.

NOAA, National Center for Environmental Information. 1999. Hazmat. report, 99–1, 1–12.

Nogawa, K. 1981. Itai-Itai disease and follow-up Studies. in Nriagu, J. (Ed.); Cadmium in the Environment, Part 11, Health Effects; John Wiley & Sons, Inc., New York.

Norouzi, S., Khademi, H., Cano, A. F., Acosta, J. A. 2016. Biomagnetic monitoring of heavy metals contamination in deposited atmospheric dust, a case study from Isfahan, Iran. J. Environ. Manage. 173, 55–64.

Novozamsky, I., Lexmond, T.M., Houba, V.J.G. 1993. A single extraction procedure of soil for evaluation of uptake of some heavy-metals by plants; Int. J. Environ. Anal. Chem. 51, 47–58.

Nziguheba, G., Smolders, E. 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci. Total Environ. 390, 53–57.

Oak Ridge National Laboratory, 2013. Risk Assessment Information System (RAIS). Available from: http://rais.ornl.gov, Accessed 25.8. 2018.

Official Gazette of Republic of Serbia, Regulation on control and certification in organic production and methods of organic production, 48/11.

Official Gazette of Republic of Serbia, Regulation on organic production and organic products, 62/06.

Official Gazette of Republic Serbia, Law on Organic Production, 30/10.

Official Gazette, Regulation on the system quality monitoring program land, indicators for risk assessment from land degradation and methodology for preparation of remediation programs, Republic of Serbia 88/2010.

Official Gazette, Regulation on the quantities of pesticides, metals and metalloids and other toxic substances, chemotherapeutics, anabolic and other substances that may be found in foods 5/92. 11/92, Republic of Serbia 5/92, 11/92.

Official Gazette Republic of Croatia 2/05 and 16/05.

Oliveira, S.R., Gomes Neto, J.A., Nóbrega, J.A., Jones, B.T. 2010. Determination of macroand micronutrients in plant leaves by high-resolution continuum source flame atomic absorption spectrometry combining instrumental and sample preparation strategies. Spectrochim. Acta. B. 65, 316–320.

Oliva, S.R., Mingorance, M.D. 2006. Assessment of airborne heavy metal pollution by aboveground plant parts. Chemosphere. 65, 177–182.

Organisation Internationale de la vigne et du vin (OIV). 2015. International Code of Oenological Practices, Annex: Maximum Acceptable Limits, Issue 2015/01. Paris, France.

Ozkul, C. 2016. Heavy metal contamination in soils around the Tuncbilek thermal power plant (Kutahya, Turkey). Environ. Monit. Assess. 188, 284.

Pacyna, J.M., Pacyna, E.G. 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, Environ. Rev. 9, 269–298.

Pagano, G., Guida, M., Tommasi, F., Oral, R. 2015. Health effects and toxicity mechanisms of rare earth elements – Knowledge gaps and research prospects. Ecotoxicol. Environ. Safety. 115, 40–48.

Pang, X., Li, D., Peng, A. 2002. Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. Environ. Sci. Pollut. Res. 9, 143–148.

Pant, P., Harrison, M.R. 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. Atmos. Environ. 77, 78–97.

Paterson, E., Sanka, M., Clark, L. 1996. Urban soils as pollutant sinks-A case study from Aberdeen, Scotland. Applied Geochemistry. 11. 129–131.

Peijnenburg, W.G.M., Zablotskaja, M., Vijver, M.G. 2007. Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction; Ecotoxocol. Environ. Saf. 67, 163–179.

Pelfrêne, A., Waterlot, C., Mazzuca, M., Nisse, C., Cuny, D., Richard, A., Denys, S., Heyman, C., Roussel, H., Bidar, G., Douay, F. 2012. Bioaccessibility of trace elements as affected by soil parameters in smelter-contaminated agricultural soils: A statistical modeling approach. Environ. Pollut. 160, 130–138.

Petrovský, E., Ellwood, B.B. 1999. Magnetic Monitoring of Air-, Land and Water Pollution. In: Maher, B.A., Thompson, R. (Eds.) Quaternary Climates, Environments and Magnetism, Cambridge University Press, Cambridge, 279–322.

Petrovský E., Kapička A., Jordanova N., Knab M. and Hoffmann V. 2000. Low-field magnetic susceptibility: a proxy method of estimating increased pollution of different environmental systems. Environ. Geol. 39, 312–318.

Petrovský, E., Zbořil, R., Grygar, T.M., Kotlík, B., Novák, J., Kapička, A., Grison, H. 2013. Magnetic particles in atmospheric particulate matter collected at sites with different level of air pollution. Stud. Geophys. Geod. 57, 755-770.

Pinto, E., Almeida, A.A., Ferreira, I.M.P.L.V.O. 2015. Assessment of metal(loid)s phytoavailability in intensive agricultural soils by the application of single extractions to rhizosphere soil. Ecotox. Environ. Safe. 113, 418–424.

Plotka-Wasylka, J., Rutkowska, M., Cieslik, B.,Tyburcy, A., Namiesnik, J. 2017. Determination of Selected Metals in Fruit Wines by Spectroscopic Techniques. ID 5283917, 1−9.

Poggio, L., Vrščaj, B., Schulin, R., Hepperle, E., Ajmone Marsan, F. 2009. Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). Environ. Pollut. 157, 680–689.

Pope, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D. 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA-J Am Med Assoc 287, 1132–1141.

Pope, C.A., Dockery, D.W. 2006. Health effects of fine particulate air pollution: lines that connect. J. Air. Waste. Manage. Assoc. 56, 709−742.

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.

Qiao, Q.Q., Huang, B.C., Zhang, C.X., Piper, J.D.A., Pan, Y.P., Sun, Y. 2013. Assessment of heavy metal contamination of dustfall in northern China from integrated chemical and magnetic investigation. Atmos. Environ. 74, 182–193.

Quevauviller, Ph., Lachica, M., Barahona, E., Rauret, G., Ure, A., Gomez, V., Muntau, H. 1996. Interlaboratory comparison of EDTA and DTPA procedures prior to certification of extractable trace elements in calcareous soil. Sci. Total Environ. 178, 127–132.

Queavauviller, P.H., Rauret, G., Ure, A., Bacon, J., Muntau, H. 1997. EUR Report 17127 EN, European Commission, Brussels.

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

Quevauviller, Ph. 2002. Operationally-defined extraction procedures for soil and sediment analysis. Part 3: New CRMs for trace element extractable contents, Trends Anal. Chem. 21, 774-785.

R Team. 2012. A language and environment for statistical computing. http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf Accessed 27.07. 2018.

Rachwał, M., Rybak, J., Rogula-Kozłowska, W. 2018. Magnetic susceptibility of spider webs as a proxy of airborne metal pollution. Environ. Poll. 234, 543–551.

Radha, R., Tripathi, R.M., Vinod, K.A., Sathe, A.P., Khandekar, R.N., Nambi, K.S.V. 1997. Assessment of Pb, Cd, Cu and Zn exposures of 10 year old children in Mumbai, Environ. Res. 80, 215 – 221.

Radulescu, C., Stihi, C., Popescu, I.V., Dulama, I.D., Chelarescu, E. D., Chilian, A. 2013. Heavy metal accumulation and translocation in different parts of *Brassica oleracea L.* Rom. J. Phys. 58, 1337–1354.

Rao, C.R.M, Sahuquillo, A., Lopez Sanchez, J. F. 2008. A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials, Water Air Soil Pollut. 189, 291–333.

Rao, C.R.M., Sahuquillo, A., Lopez-Sanchez, J.F. 2010. Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. Anal. Chim. Acta. 662, 128–136.

Relić, D., Đorđević, D., Popović, A., Blagojević, T. 2005. Speciations of trace metals in the Danube alluvail sediments within an oil refinery, Envrion. Int. 31, 661-669.

Relić, D., Đorđević, D., Popović, A., Jadranin, M., Polić, P. 2010. Fractionation and potential mobility of trace metals in Danube alluvial aquifer within an industrialzed zone, Envrion. Monit. Assess. 171, 229-248.

Relić, D., Đorđević, D., Sakan, S., Anđelković, I., Pantelić, A., Stanković, R., Popović, A. 2013. Conventional, micorwave, and ultrasound sequential extractions for the fractionation of metals in sediments within the Petrochemical Industry, Serbia, Envrion. Monit. Assess. 185, 7627-7645.

Republic Hydrometeorological Service of Serbia (http://www.hidmet.gov.rs/) Accessed 20.07.2018.

Ribolzi, O., Valles, V., Gomez, L., Voltz, M. 2002. Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment. Environ. Pollut. 117, 261–71.

Rinklebe, J., Kumpiene, J., Du Laing, G., Ok, Y.S. 2017. Biogeochemistry of trace elements in the environmenteeditorial to the special Issue. J. Environ. Manage. 186, 127-130.

Ristić, M., Perić-Grujić, A., Antanasijević, D., Ristić, M., Aničić Urošević, M., Tomašević, M. 2013. Plants as Monitors of Lead Air Pollution. In: Lichtfouse, E., Schwarzbauer, J., Robert, D. (Eds.) Pollutant Diseases, Remediation and Recycling. Springer International Publishing Switzerland.

Rucandio, I.M., Petit-Domíngez, D.M., Fidalgo-Hijano, C., García-Gimenéz, R. 2011. Biomonitoring of chemical elements in an urban environment using arboreal and bush plant species. Environ. Sci. Pollut. Res. 18, 51–63.

Rühling, Å., Tyler, G. 1968. An ecological approach to lead problem. Bot. Notiser. 121, 321−342.

Sakamoto, M., Nakano, A., Akagi, H. 2001. Declining Minamata male birth ratio associated with increased male fetal death due to heavy methylmercury pollution; Environ. Res. 87, 92–98.

Sakan, S., Dević, G., Relić, D., Anđelković, I., Sakan, N., Đorđević, D., 2014. Environmental assessment of heavy metal pollution in freshwater sediment, Serbia. Clean. 42, 1–8.

Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., Klein, P., ´ Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.A., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandstrom, H., Siewers, U., Steenfelt, A., Tarvainen, T. Geochemical Atlas of Europe, Part 1, Background Information, Methodology and Maps. Geological Survey of Finland: Espoo, 2005. (http://weppi.gtk.fi/publ/foregsatlas/).

Salo, H. 2017. Magnetic air quality monitoring using cryptogams. In: Aničić Urošević, M., Vuković G., Tomašević, M. (Eds.), Biomonitoring of Air Pollution Using Mosses and Lichens, A Passive and Active Approach, State of the Art Research and Perspectives. Nova Science Publishers, New York, NY.

Salo, H., Berisha, A.K., Mäkinen, J. 2016. Seasonal comparison of moss bag technique against vertical snow samples for monitoring atmospheric pollution. J. Environ. Sci. 41, 128–137.

Santos, S., Costa, C.A.E., Duarte, A.C., Scherer, H.W., Schneider, R.J., Esteves, V.I., Santos, E.B.H. 2010. Influence of different organic amendments on the potential availability of metals from soil: A study on metal fractionation and extraction kinetics by EDTA. Chemosphere. 78, 389–396.

Sánchez-Rodas, D., Alsioufia, L., Sánchez de la Campaa, A.M., González-Castanedoa, Y. 2017. Antimony speciation as geochemical tracer for anthropogenic emissions of atmospheric particulate matter. Journal of Hazardous Materials. 324, 213–220.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atm. Environ. 30, 3837–3855.

Schwarze, P.E., Øvrevik, J., Låg, M., Refsnes, M. Nafstad, P., Hetland, R.B., Dybing, E. 2006. Particulate matter properties and health effects: consistency of epidemiological and toxicological studies. Hum. Exp. Toxicol. 25, 559−579.

Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A. 1997. Reference materials for large scale metal deposition surveys. Accred. Qual. Assur, 2, 243–249.

Storer, D. A. 1984. A simple high-sample-volume ashing procedure for determination of soil organic matter. Commun. Soil. Sci. Plant. Anal. 15, 759–772.

Sumner, M.E., Miller, W.P. 1996. Cation exchange capacity and exchange coefficients. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3—Chemical Methods. SSSA, Madison, WI, 1201–1229.

Suárez, N. 2010. Leaf lifetime photosynthetic rate and leaf demography in whole plants of Ipomoea pes-caprae growing with a low supply of calcium, a 'non-mobile' nutrient, J. Exp. Bot. 61, 843–855.

Sylvain, B, Mikael, M. H., Florie, M., Emmanuel, J., Marilyne, S., Sylvain, B., Domenico, M. 2016. Phytostabilization of As, Sb and Pb by two willow species (*S. viminalis* and *S. purpurea*) on former mine technosols. Catena. 136, 44–52.

Szolnoki, Z., Farsang, A. 2013. Evaluation of metal mobility and bioaccessibility in soils of urban vegetable gardens using sequential extraction. Water Air Soil Pollut. 224, 1737.

Tack, F.M.G. 2010. Trace Elements: General Soil Chemistry, Principles and Processes. In: Hooda (Ed.) Trace elements in soil. A John Wiley and Sons, Ltd., Publication, United Kingdom.

Thiesson, J., Boulonne, L., Buvat, S., Jolivet, C., Ortolland, B., Saby, N. 2012. Magnetic properties of the French soil monitoring network: first results. Near Surface Geoscience 2012 - 18th European Meeting of Environmental and Engineering Geophysics Paris, France, pp. 3–5.

Teeling, H., Cypionka, H. 1997. Microbial degradation of tetraethyl lead in soil monitored by microcalorimetry; Appl. Microbiol. Biotechnol. 48, 275–279.

Templeton, D.M., Ariese, F., Cornelis, R., Danielsson, L.G., Muntau, H., Van Leeuwen, H.P.L.R. 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations. Pure Appl. Chem. 72, 1453–1470.

Tepanosyan, G., Maghakyan, N., Sahakyan, L., Saghatelyan A. 2017a. Heavy metals pollution levels and children health risk assessment of Yerevan kindergartens soils. Ecotoxicol. Environ. Saf. 142, 257−265.

Tepanosyan, G., Sahakyan, L., Belyaeva, O., Maghakyan, N., Saghatelyan, A. 2017b. Human health risk assessment and riskiest heavy metal origin identification in urban soils of Yerevan, Armenia. Chemosphere. 184, 1230−1240.

Thomas, E.Y, Omueti, J. A.I., Ogundayomi, O. 2012. The Effect of Phosphate Fertilizer on Heavy Metal in Soils and Amaranthus Caudatus, Agric. Biol. J. N. Am. 3, 145–149.

Thompson, F., Oldfield, R. 1986. Environmental magnetism, Quat. Sci. Rev. 6, 71–72.

Thron, R.W. 1996. Direct and indirect exposure to air pollution. Otolaryngol. Neck. Surg. 114.

Tomašević, M., Rajšić, S., Đorđević, D., Tasić, M., Krstić, J., Novaković, V. 2004. Heavy metals accumulation in tree leaves from urban areas. Environ. Chem. Lett. 2,151–154.

Tomašević, M., Vukmirović, Z., Rajšić, S., Tasić, M., Stevanović, B. 2005. Characterization of trace metal particles deposited on some deciduous tree leaves in an urban area. Chemosphere. 61, 753–760.

Tomašević, M., Antanasijević, D., Aničić, M., Deljanin, I., Perić-Grujić, A., Ristić, M. 2013. Lead concentrations and isotope ratios in urban tree leaves. Ecol. Indic. 24, 504–509.

Turan, D., Kocahakimoglu, C., Kavcar, P., Gaygısız, H., Atatanir, L., Turgut, C., Sofuoglu, C.S. 2011. The use of olive tree (Olea europaea L.) leaves as a bioindicator for environmental pollution in the Province of Aydın, Turkey. Environ Sci Pollut Res 18, 355–364.

Tyler, G. 2004. Rare earth elements in soil and plant systems - a review. Plant Soil. 267, 191–206Tyler, G., Olsson, T. 2005. Rare earth elements in forest-floor herbs as related to soil conditions and mineral nutrition. BTER 106, 177–192.

.UniQuant, 2015. <http://www.uniquant.com/>, Thermo Fisher Scientific Inc., August 24, 2015.

Urbat, M., Lehndorff, E., Schwark, L. 2004. Biomonitoring of air quality in the Cologne conurbation using pine needles as a passive sampler-Part I: Magnetic properties. Atmos. Environ. 38, 3781–3792.

Ure, A. M. 1996. Single extraction schemes for soil analysis and related applications. Sci. Total Environ., 178, 3−10.

US EPA (United States Environmental Protection Agency) 3050b, 1996. Method, Acid digestion of sediments, sludges, and soils, USEPA, Washington, DC, USA.

US EPA (United States Environmental Protection Agency), 2007. Framework for Metals Risk Assessment, EPA 120/R-07/001, Office of the Science Advisor Risk Assessment Forum U.S. Environmental Protection Agency Washington, DC 20460.

US EPA (United States Environmental Protection Agency), 2012. Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues. EPA 600/R-12/572.

Vanderpoorten, A., Goffi net, B. 2009. Introduction to Bryophytes. Ed. Cambridge University Press, New York.

Vázquez Vázquez, F.A., Pérez Cid, B., Río Segade, S. 2016. Assessment of metal bioavailability in the vineyard soil-grapevine system using different extraction methods. Food Chem., 208, 199–208.

Verosub, K., Roberts, A. 1995. Environmental Magnetism: Past, Present, and Future. J Geophys. *Res.* Atmos. 100, 2175–2192.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wåhlin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R. 2008. Source apportionment of particulate matter in Europe: a review of methods and results. Aerosol Sci. 39, 827–849.

Vuković G., Aničić Urošević M., Razumenić I., Goryainova Z., Frontasyeva M., Tomašević M., Popović A. 2013. Active Moss Biomonitoring of Small-Scale Spatial Distribution of Airborne Major and Trace Elements in the Belgrade Urban Area, Environ. Sci. Pollut. Res. 20, 5461–70.

Vuković G., Aničić Urošević M., Razumenić I., Kuzmanoski M., Pergal M., Škrivanj S., Popović A. 2014. Air quality in urban parking garages (PM10, major and trace elements, PAHs): Instrumental measurements vs. Active moss biomonitoring, Atmosp. Environ. 85, 31–40.

Vuković, G., Aničić Urošević, M., Goryainova, Z., Pergal, M., Škrivanj, S., Samson, R., Popović, A., 2015a. Active moss biomonitoring for extensive screening of urban

air pollution: magnetic and chemical analyses. Sci. Total Environ. 521–522, 200–210.

Vuković, G., Urošević, M. A., Tomašević, M., Samson, R., Popović, A. 2015b. Biomagnetic monitoring of urban air pollution using moss bags (Sphagnum girgensohnii). Ecol. Indic. 52, 40–47.

Vuković, G., Aničić Urošević, M., Škrivanj, S., Milićević, T., Dimitrijević, D., Tomašević, M., Popović, A. 2016. Moss bag biomonitoring of airborne toxic element decrease on a small scale: a street study in Belgrade, Serbia. Sci. Total. Environ. 542, 394–403.

Vuković, G., Aničić Urošević, M., Škrivanj, S., Vergal K., Tomašević, M., Popović, A. 2017. The first survey of airborne trace elements at airport using moss bag technique. Environ. Sci. Pollut. Res. 24, 15107–15115.

Vyas, B., Kumar Singh, A., Singh Cameotra, S. 2015. Sorption behaviour of maneb in the agriculture soils and its correlation with soil properties, IJSER.IN. 1, 1−8.

Vystavna, Y., Rushenko, L., Diadin, D., Klymenko, O., Klymenko, M. 2014. Trace metals in wine and vineyard environment in southern Ukraine. Food Chem. 146, 339–344.

Vystavna, Y., Rätsep, R., Klymenko, N., Drozd, O., Pidlisnyuk, V., Klymenko, M. 2015. Comparison of soil-to-root transfer and translocation coefficients of trace elements in vines of Chardonnay and Muscat white grown in the same vineyard. Sci. Hortic. − Amsterdam. 192, 89−96.

Wang, G., Oldfield, F., Xia, D., Chen, F., Liu, X., Zhang, W. 2012. Magnetic properties and correlation with heavy metals in urban street dust: A case study from the city of Lanzhou, China. Atmos. Environ. 46, 289–298.

Wang, B., Xia, D.S., Yu, Y., Jia, J., Xu, S.J. 2013. Magnetic records of heavy metal pollution in urban topsoil in Lanzhou, China. Chin. Sci. Bull. 158, 384–395.

Wang, B., Xia, D., Yu, Y., Cheng, H., Jia, J. 2018. Source apportionment of soil-contamination in Baotou City (North China) based on a combined magnetic and geochemical approach. Sci. Total Environ. 642, 95–104.

Wang, G., Ren, F., Chen, J., Liu, Y., Ye, F., Oldfield, F., Zhang, W., Zhang, X. 2017. Magnetic evidence of anthropogenic dust deposition in urban soils of Shanghai, China. Chem. Erde. 77, 421–428.

Wehrens, R., Kruisselbrink, J. 2017. Supervised and Unsupervised Self Organising Maps, Package 'Kohonen'; https://cran.r project.org/web/packages/kohonen/kohonen.pdf. Accessed 24.08.2018.

Weiss, P., Offenthaler, I., Öhlinger, R., Wimmer, J. 2003. Higher plants as accumulative bioindicators. In: Markert, B., Breure, A.M., Zechmeister, H.G. (eds) Bioindicators & Biomonitors, Principles, Concepts and Applications. Elsevier, Amsterdam. 6, 465–500.

Wen, B., Yuan, D., Shan, X., Li, F., Zhang, S. 2001. The influence of rare earth element fertilizer application on the distribution and bioaccumulation of rare earth elements in plants under field conditions. Chem. Spec. Bioavailab. 13, 39−48.

WHO (World Health Organization), 2005. Air quality guidelines (http://www.euro.who.int). ISBN 92 890 2192 6.

WHO (World Health Organization), 2006. Air quality guidelines. Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Druckpartner Moser, Germany.

WHO (World Health Organisation), 2016. http://www.who.int /; Accessed 27.08.2018.

WHO (World Health Organisation), 2018. http://www.who.int; Accessed 26.08.2018.

Wightwick, M.A., Mollah, R.M., Partington, L.D., Allinson, G., 2008. Copper Fungicide Residues in Australian Vineyard Soils, J. Agric. Food Chem., 56, 2457–2464.

Wierzbowska, J., Sienkiewicz, S., Krzebietke, S. and Bowszys, T. 2016. Heavy metals in water percolating through soil fertilized with biodegradable waste materials, Water. Air. Soil Pollut. 227, 1−10.

Wolterbeek, B. 2002. Biomonitoring of trace element air pollution: principles, possibilities and perspectives. Environ. Pollut.120,11–21.

Wuana, R.A., Okieimen, F.E. 2011. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. ISRN Ecology, Article ID 402647, 1–20.

Yaqin, J., Yinchang, F, Jianhui, W., Tan, Z., Zhipeng, B., Chiqing, D. 2008. Contamination features and health risk of soil heavy metals in China. Sci. Total Environ. 5, 571–578

Yin, G., Hu, S., Cao, L., Roesler, W., Appel, E. 2013. Magnetic properties of tree leaves and their significance in atmospheric particle pollution in Linfen City, China. Chin. Geogr. Sci. 23, 59–72.

Zhang, S., Shan, S. 2001. Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application, Environ. Pollut. 112, 395–405.

Zhang, J., Liu, C.L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China – weathering features, anthropogenic impact and chemical fluxes. Estuar. Coast. Shelf. Sci. 54, 1051–1070.

Zhang, C., Huang, B., Li, Z., Lu, H. 2006. Magnetic properties of high-road-side pine tree leaves in Beijing and their environmental significance. Chin. Sci. Bull. 51, 3041–3052.

Zhang, C.X., Qiao, Q.Q., John, D.A., Huang, B.C. 2011. Assessment of heavy metal pollution froma Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods. Environ. Pollut. 159, 3057–3070.

Zhang, C.X., Qiao, Q.Q., Appel, E.; Huang, B.C. 2012. Discriminating 1630 sources of anthropogenic heavy metals in urban street dusts using magnetic and chemical methods. J. Geochem. Explor. 119–120, 60–75

Zhou, Q., Zhang, J., Fu, J., Shi, J., Jiang, G. 2008 Biomonitoring: an appealing tool for assessment of metal pollution in the aquatic ecosystem. Anal. Chim. Acta. 606, 135–150.

http://www.nsseme.com/en/, Assessed 21.08.2018.

http://www.plavinci.rs, Assessed 21.08.2018.

8 Appendix

8.1 Appendix 1: Experimental part

Figure 8.1.1 a) distillatior for preparing acid (p.a.) for the samples digestion; b) distillatior for preparing ultra-pure water used for the samples preparation; c) pH-meter d) dryer; e) centrifuge.

Table 8.1.1: The measured elements' concentration and magnetic parameters through the experiments in this doctoral dissertation

Sample	Determined elements' concentration and magnetic parameters
Experiment 1	
Soil extracts	Al, Fe, K, Mn, Na, P, S, Si, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn
Soil pseudo-total	Al, Fe, K, Mn, Na, P, S, Si, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn
plant material	Al, Cd, Cr, Cu, Fe, K, Ni, Pb, Zn
Experiment 2	
Soil extracts	Al, As, B, Ba, Be, Ca, Cd, Co, C,, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sr, V, Zn
Soil pseudo-total	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sr, V, Zn
Plant material	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sr, V, Zn
Experiment 3	
Soil extracts	Al, As, B, Ba, Be, Ca, Cd, Co, C,, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sr, V, Zn
Soil pseudo-total	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sr, V, Zn
Plant material	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, V, Zn
Experiment 4	
Moss material	Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, La, Li, Lu, Mg, Mn, Nd, Ni, Pb, Pr, Sb, Sc, Sm, Sn, Sr, Tb, Rh, Ti, Tm, V, Y, Zn
Plant material	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, V, Zn
Experiment 5	
Soil extracts	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sr, V, Zn
Soil pseudo-total	Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sr, V, Zn
Plant material	Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sr, V, Zn
Moss material	Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sr, V, Zn
Experiment 6	
Soil Uniquant	Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, S, Si, Sr, Ti, V, Zn, Zr
Plant Uniquant	Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Rb, S, Si, Sr, Ti, Zn
Soil and plant magnetic parameters	SIRM, χ

Table 8.1.2: Limit of detection (LOD) (µg L^{-1}) and limit of quantification (LOQ) (µg L^{-1}) of the method for determination element concentrations in the soil extracts using ICP-OES (Experiments 1, 2, 3 and 5)

element	2 h H_2O		16 h H_2O		$CaCl_2$		NH_4NO_3		Na_2EDTA		CH_3COOH	
λ (nm)	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
Al 394.4	2.68	8.94	3.65	12.17	3.7	12.34	1.93	6.42	3.46	11.53	5.28	17.59
Al 396.1	2.28	7.59	1.16	3.86	1.42	4.74	1.05	3.5	1.47	4.92	2.78	9.27
As 189.0	1.43	4.78	1.59	5.31	1.17	3.89	1.18	3.92	1.59	5.29	1.41	4.72
B 208.9	0.75	2.49	0.56	1.88	0.49	1.63	0.5	1.68	0.63	2.09	0.71	2.36
B 249.7	0.57	1.90	0.59	1.96	0.41	1.36	0.44	1.46	/	/	0.54	1.79
Ba 493.4	0.08	0.26	0.22	0.73	0.07	0.24	0.07	0.23	/	/	0.26	0.84
Ba 455.4	/	/	/	/	/	/	/	/	0.04	0.14	/	/
Be 234.8	0.06	0.19	0.17	0.56	0.06	0.18	0.06	0.20	0.07	0.23	0.06	0.17
Ca 315.8	/	/	/	/	/	/	/	/	0.94	3.12	/	/
Ca 317.9	0.49	1.62	1.70	5.66	/	/	0.49	1.63	/	/	/	/
Ca 373.6	2	6.67	17.33	57.77	/	/	2.14	7.13	/	/	0.79	2.62
Cd 214.4	/	/	/	/	/	/	/	/	0.13	0.45	/	/
Cd 226.5	0.09	0.30	0.08	0.26	0.06	0.2	0.06	0.20	0.08	0.28	0.09	0.29
Cd 228.8	0.14	0.46	0.31	1.04	0.13	0.42	0.13	0.44	/	/	0.13	0.43
Co 230.7	0.30	1.01	0.77	2.56	0.27	0.9	0.27	0.9	0.41	1.37	0.24	0.78
Co 231.1	0.37	1.25	0.88	2.93	0.33	1.1	0.33	1.10	0.50	1.66	0.33	1.11
Cr 205.5	0.16	0.52	0.16	0.52	0.18	0.59	0.16	0.53	0.19	0.62	0.16	0.51
Cu 213.5	0.38	1.26	0.361	1.19	0.36	1.2	0.32	1.07	0.41	1.38	0.28	0.94
Cu 224.7	/	/	/	/	/	/	/	/	0.56	1.86	/	/
Cu 324.7	0.28	0.93	0.53	1.77	0.38	1.27	0.34	1.35	/	/	0.36	1.17
Fe 238.2	0.74	2.46	0.52	1.73	0.37	1.23	0.36	1.19	0.47	1.56	0.68	2.27
Fe 259.9	0.59	1.96	0.45	1.49	0.31	1.03	0.3	1	0.4	1.32	0.55	1.83
K 766.4	0.82	2.72	1.33	4.45	0.38	1.26	0.42	1.39	0.38	1.28	1.03	3.45
K 769.8	0.98	3.26	1.52	5.06	0.6	1.99	0.67	2.23	0.65	2.17	1.22	4.05
Li 670.7	0.02	0.06	0.01	0.04	0.01	0.04	0.01	0.04	0.02	0.06	0.02	0.08
Mg 279.0	2.58	8.61	4.12	13.72	2.99	9.96	2.81	9.36	3.83	12.78	2.32	7.73
Mn 257.6	0.11	0.37	0.09	0.31	0.07	0.25	0.07	0.25	0.08	0.26	0.09	0.32
Mn 259.3	/	/	/	/	/	/	/	/	0.1	0.34	/	/
Mn 260.5	0.18	0.59	0.16	0.51	0.20	0.66	0.18	0.6	/	/	0.2	0.68
Na 589.5	0.15	0.50	0.66	2.17	0.21	0.68	0.13	0.43	/	/	0.28	0.94
Ni 231.6	0.31	1.03	0.33	1.10	0.24	0.8	0.23	0.78	0.33	1.11	0.3	1.01
P 177.4	2.66	8.84	1.76	5.86	1.59	5.3	1.59	5.29	2.44	8.14	2.78	9.26
P 178.2	/	/	/	/	/	/	/	/	2.91	9.71	/	/
P 185.9	3.95	13.17	4.16	13.88	4.56	15.18	4.23	14.11	/	/	3.56	11.86
Pb 220.3	1.35	4.50	1.15	3.82	0.88	2.93	0.87	2.89	1.23	4.11	1.36	4.52
S 182.0	4.12	13.73	4.48	14.93	4.90	16.32	4.65	15.5	/	/	/	/
S 182.6	14.97	49.89	11.93	39.77	11.18	37.26	18.01	60.03	14.77	49.24	14.82	49.39
Sb 217.5	4.20	13.20	2.49	8.29	1.76	5.84	1.71	5.71	1.81	5.98	4.3	14.33
Sr 421.5	0.03	0.09	0.14	0.46	0.02	0.08	0.02	0.08	0.03	0.11	0.02	0.07
V 292.4	0.56	1.86	0.54	1.81	0.41	1.37	0.39	1.3	0.44	1.47	0.56	1.85
Zn 213.8	0.08	0.26	0.17	0.57	0.07	0.24	0.08	0.26	0.21	0.69	0.07	0.23

Table 8.1.3: Limit of detection (LOD) (μg L^{-1}) and limit of quantification (LOQ) (μg L^{-1}) of the method for determination the pseudo-total element concentrations in the soil using ICP-OES (Experiments 1, 2, 3 and 5)

element λ (nm)	LOD	LOQ
Al 394.4	2.10	7.01
Al 396.1	0.87	2.9
As 189.0	2.43	8.09
As 193.8	2.91	9.7
As 197.30	5.63	18.77
B 208.9	0.89	2.98
B 249.7	2.44	8.13
Ba 493.4	9.04	30.00
Be 234.8	0.20	0.67
Bi 223.1	5.48	18.26
Ca 315.8	0.75	2.52
Ca 3117.9	0.51	1.7
Ca 373.6	1.88	6.29
Cd 214.4	0.08	0.26
Cd 226.5	0.13	0.43
Cd 228.8	0.32	1.06
Co 228.6	0.46	1.53
Co 230.8	0.77	2.56
Co 231.1	0.94	3.13
Cr 205.5	0.29	0.96
Cr 267.7	1.77	5.91
Cu 213.5	0.76	2.54
Cu 224.7	0.68	2.28
Fe 238.2	0.37	1.26
Fe 239.5	0.47	1.58
Fe 259.9	0.38	1.27
K 766.4	0.32	1.09
K 769.8	0.67	2.25
Li 670.7	0.42	1.41
Mg 279.0	3.18	10.6
Mg 280.2	0.02	0.08
Mg 285.2	0.12	0.43
Mn 257.6	0.06	0.22
Mn 259.3	0.09	0.30
Mn 260.5	0.15	0.50
Mo 202.0	0.41	1.36
Na 589.5	0.15	0.50
Ni 221.6	0.54	1.80
Ni 231.6	0.61	2.04
P 177.4	3.50	11.67
P 178.2	4.19	13.98
P 185.9	6.27	20.9
Pb 220.3	2.3	7.68
S 180.7	4.55	15.17
Sb 206.8	2.35	7.82
Sb 217.5	4.17	13.9
Sr 407.7	1.62	3.87
Sr 421.5	5.56	18.5
V 292.4	27.89	92.00
Zn 206.2	0.18	0.60
Zn 213.8	0.15	0.50

Table 8.1.4: Limit of detection (LOD) (µg L^{-1}) and limit of quantification (LOQ) (µg L^{-1})of the method for determination element concentrations in the plant material (seed, pulp, skin, petiole and leaf) (Experiments 1, 2, 3 and 5) and the moss material (Experiment 4 and 5) using ICP-OES

element	grapevine material		moss material	
λ (nm)	LOD	LOQ	LOD	LOQ
Al 167.1	0.49	1.63	0.36	1.20
Al 308.2	3.38	11.27	1.85	6.17
Al 394.4	2.25	7.50	2.59	8.63
Al 396.1	0.93	3.09	0.74	2.46
As 189.0	1.37	4.58	1.59	5.31
As 193.8	1.87	6.22	1.64	5.47
As 197.3	2.53	8.46	2.4	8.01
B 208.9	0.48	1.61	0.44	1.48
B 249.8	0.44	1.46	0.43	1.46
Ba 455.4	0.04	0.12	0.03	0.09
Ba 493.4	0.09	0.31	0.07	0.24
Be 234.9	0.06	0.21	0.06	0.19
Bi 223.1	2.48	8.27	1.87	6.25
Ca 315.9	1.22	4.07	0.9	2.99
Ca 317.9	0.67	2.22	0.54	1.79
Ca 373.7	2.84	9.46	1.88	6.27
Cd 214.4	0.06	0.21	0.05	0.18
Cd 226.5	0.07	0.23	0.06	0.21
Cd 228.8	0.2	0.67	0.16	0.54
Co 228.6	0.24	0.80	0.19	0.62
Co 230.8	0.30	0.99	0.24	0.81
Co 238.9	0.60	2.00	0.49	1.64
Cr 205.6	0.20	0.67	0.15	0.48
Cr 267.7	0.38	1.26	0.33	1.10
Cu 213.6	0.35	1.16	0.3	0.99
Cu 217.9	1.63	5.43	1.51	5.03
Cu 224.7	0.50	1.56	0.37	1.23
Cu 324.8	0.37	1.24	0.03	0.99
Fe 238.2	0.40	1.33	0.36	1.96
Fe 239.6	0.60	1.98	0.52	1.74
Fe 259.9	0.49	1.63	0.31	1.03
K 766.5	0.58	1.92	0.44	1.45
K 769.9	0.80	2.68	0.77	2.57
Li 670.8	0.01	0.04	0.01	0.05
Mg 279.6	0.01	0.05	0.01	0.04
Mg 280.3	0.02	0.08	0.02	0.07
Mg 285.2	0.16	0.54	0.18	0.58
Mn 257.6	0.06	0.19	0.06	1.18
Mn 259.4	0.08	0.25	0.06	0.21
Mn 260.6	0.19	0.65	0.14	0.45
Na 588.9	0.21	0.68	0.017	0.56
Ni 221.6	0.43	1.43	0.21	0.71
Ni 231.6	0.28	0.94	0.26	0.87
Ni 232.0	0.86	2.87	1.03	3.42
Pb 220.3	0.87	2.90	0.79	2.64
Sb 217.6	2.06	6.88	1.63	5.43
Sr 407.8	0.01	0.05	0.01	0.04
Sr 421.6	0.03	0.08	0.02	0.07
V 292.4	0.41	1.36	0.44	1.48
Zn 202.5	0.06	0.22	0.07	0.23
Zn 206.2	0.09	0.30	0.09	0.30
Zn 213.6	0.10	0.34	0.08	0.27

Table 8.1.5: Limit of detection (LOD) (μg L^{-1}) of the method for determination element concentrations in the plant material (seed, pulp, skin, petiole and leaf) (Experiments 1, 2, 3 and 5) and moss material (Experiment 4 and 5) busing ICP-MS

element λ (nm)	Plant material	Moss material	element λ (nm)	Plant material	Moss material
μg L^{-1}	LOD	LOD	μg L^{-1}	LOD	LOD
6Li	0.2231	0.0041	85Rb	0.0457	0.0405
9Be	0.0037	0.0027	121Sb	0.0383	0.0123
45Sc	0.0349	0.0907	123Sb	0.0193	0.0112
51V	0.0195	0.0247	151Eu	0.0011	0.0008
52Cr	0.0223	0.0211	153Eu	0.0010	0.0010
53Cr	0.0343	0.0913	158Gd	0.0034	0.0019
59Co	0.0067	0.0103	160Gd	0.0014	0.0015
71Ga	0.0358	0.0200	159Tb	0.0025	0.0014
75As	0.0192	0.0430	161Dy	0.0019	0.0021
89Y	0.0058	0.0050	163Dy	0.0022	0.0017
97Mo	0.0248	0.0256	164Dy	0.0022	0.0016
98Mo	0.0110	0.0123	165Ho	0.0013	0.0005
101Ru	0.0030	0.0028	166Er	0.0013	0.0008
102Ru	0.0045	0.0017	167Er	0.0019	0.0008
111Cd	0.0241	0.0305	168Er	0.0020	0.0007
114Cd	0.0160	0.0188	169Tm	0.0008	0.0001
115In	0.0043	0.0059	171Yb	0.0018	0.0010
139La	0.0069	0.0055	172Yb	0.0016	0.0012
140Ce	0.0083	0.0089	173Yb	0.0016	0.0017
141Pr	0.0220	0.0011	174Yb	0.0021	0.0010
143Nd	0.0048	0.0041	175Lu	0.0011	0.0004
145Nd	0.0130	0.0073	203Tl	0.0174	0.0061
146Nd	0.0050	0.0040	205Tl	0.0048	0.0028
147Sm	0.0041	0.0015	206Pb	0.0654	0.1026
149Sm	0.0023	0.0026	207Pb	0.0729	0.1123
152Sm	0.0036	0.0019	208Pb	0.0358	0.1037
154Sm	0.0031	0.0019	209Bi	0.0123	0.0100
47Ti	0.6449	0.8780	232Th	0.0038	0.0016
49Ti	0.8001	1.0397			

Table 8.1.6: Recovery (%) of measured elements in the soil extracts obtained using BCR 483 CRM

BCR 483	Cd	Cr	Cu	Ni	Pb	Zn
			0.44 mol L^{-1} CH_3COOH			
Experiment 5	87	81	92	95	91	103
			0.01 mol L^{-1} $CaCl_2$			
Experiment 1	116	139	132	126	78	131
Experiment 2	112	121	125	120	81	128
Experiment 3	109	120	120	117	81	125
Experiment 5	108	118	120	108	80	121
			0.1 mol L^{-1} NH_4NO_3			
Experiment 1	78	90	84	78	81	83
Experiment 2	77	112	80	72	75	76
Experiment 3	81	98	91	81	78	99
Experiment 5	81	122	87	85	82	79
			0.05 mol L^{-1} Na_2EDTA			
Experiment 1	122	130	118	135	132	115
Experiment 2	118	128	120	130	131	110
Experiment 3	118	125	119	128	125	108
Experiment 5	111	115	103	109	118	103

Table 8.1.7: Recovery (%) of measured pseudo-total element concentrations in the soil obtained using CRMs (2711a, SARM 42 SAVM, ERM CC 135a and BCR 143 R)

	Experiment 1	Experiment 2	Experiment 3	Experiment 5	Experiment 6
			2711 a		
Al		61	62	65	
As		87	86	88	
Ba		67	65	72	
Ca		80	75	83	
Cd		88	87	91	
Co		82	81	86	
Cr		70	68	72	
Cu		96	92	96	
Fe		93	91	95	
K	NA	59	56	61	NA
Mg		82	80	87	
Mn		95	93	96	
Na		51	56	59	
Ni		94	91	95	
P		87	85	88	
Pb		91	89	96	
Sr		70	68	78	
V		94	91	99	
Zn		88	87	91	
			SARM 42 SAVM		
Ba		65	65	67	
Co		72	72	75	154
Cu		118	115	118	123
Mo					ND
Ni	NA	78	81	79	121
Pb		115	118	115	ND
Sr		109	107	103	97
V		68	72	75	113
Zn		72	72	75	102
			ERM CC 135 a		
Al	115	120	118	106	
Ba	130	120	121	118	
Be	121	120	120	118	
Ca	107	106	108	107	
Co	71	99	102	106	
Cr	122	118	118	116	
Cu	108	106	108	109	
Fe	80	117	116	113	NA
K	85	90	90	91	
Mg	129	122	120	121	
Mn	121	125	118	112	
Na	108	112	112	110	
Ni	73	82	101	88	
Pb	97	100	99	99	
V	125	128	121	120	
Zn	94	97	97	99	
			BCR 143 R		
Cd		81	81	82	134
Co		106	104	101	175
Cr		83	88	92	ND
Cu	NA	101	91	80	114
Mn		107	107	106	119
Ni		79	82	85	117
Pb		78	79	83	97
Zn		102	102	110	113

NA−not analysed; ND−not detected

Table 8.1.8: Range of recovery (%) of the measured element concentrations in the plant and moss material obtained by CRMs (MOSS2−M2 and MOSS3−M3)

	Recovery %		Exceptions %	
	MOSS2	MOSS3	MOSS2	MOSS3
Experiment 1 plant	70−120	71−119	Cr (61%)	Ni (69%), Cr (67%)
Experiment 2 plant	70−120	70−120	Cr (69%)	Cr (69%)
Experiment 3 plant	71−116	70−120		Cr (69%)
Experiment 4 moss and leaves	75−102	75−116	Cr (68%), La (71%); Ce (65%)	Th (55%)
Experiment 5 plant and moss	80−105	85−118	La (73%); Ce (68%)	Th (62%)
Experiment 6 leaf	ND	ND		

ND−the concentrations in CRM were not detected

8.2 Appendix 2: Experiment 1

Table8.2.1: Descriptive statistics (Median−M, Standard Deviation–SD, Minimum–Min and Maximum–Max) of the element concentrations (mg kg^{-1}, *µg kg^{-1}) extracted from the topsoil samples from the experimental vineyard (Experiment 1; Milićević et al., 2017a)

		Al	Fe	K	Mn	Na	P	S	Si	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
Single extraction																		
CH_3COOH	M	45	16	66	24	41	77	36	220	0.06	0.05	0.08	1.9	0.1	0.8	51.2*	0.02	1.0
	SD	11	14	15	5	7.2	70	19	28	0.02	0.04	0.02	1.2	0.2	0.3	0.6*	0.02	1.2
	Min	27	5.6	49	20	30	14	14	170	0.04	0.01	0.06	0.4	0.0	0.5	49.9*	0.01	0.0
	Max	59	49	88	35	50	200	74	260	0.08	0.11	0.11	4.3	0.4	1.2	51.6*	0.05	3.7
16 h H_2O	M	25	22	7.7	0.3	13	3.8	27	58	3.9*	4.0*	0.03	1.1	16*	0.1	0.1	0.06	0.6
	SD	5.8	5.3	2	0.2	4.5	1.8	8.4	12	1.0*	2.4*	0.02	0.9	7.9*	0.2	0.2	0.02	0.5
	Min	15	14	5.9	0.2	9.2	2.1	20	37	2.3*	0.9*	0.01	0.3	3.5*	0.0	0.0	0.04	0.0
	Max	33	31	11	0.6	22	7.2	46	73	5.6*	7.7*	0.04	2.6	26*	0.4	0.4	0.07	1.6
2 h H_2O	M	35	20	7.14	0.06	15	5.1	10	88	0.253*	6.7*	0.04	1.3	17*	0.3	0.04	0.10	0.4
	SD	20	12	2.6	0.03	4	1.9	5.5	46	0.003*	4.5*	0.03	0.3	6.8*	0.1	0.03	0.06	0.3
	Min	16	6.2	3.5	0.02	11	3.2	2.5	17	0.249*	1.7*	0.02	0.9	3.6*	0.2	0.02	0.06	0.2
	Max	79	44	11	0.1	23	8.9	19	140	0.256*	15*	0.11	1.8	29*	0.6	0.09	0.22	0.9
Na_2EDTA	M	16	100	89	78	**	20	4.3	167	0.08	0.6	0.04	16	19*	1.3	2.6	0.1	2.0
	SD	12	54	25	55	**	14	1.7	128	0.04	0.6	0.04	8.0	9.9*	0.8	1.1	0.2	1.5
	Min	2.3	39	52	14	**	1.9	1.4	44	0.03	0.0	0.00	4.1	2.6*	0.3	1.3	0.0	0.8
	Max	42	190	132	190	**	36	7.4	463	0.16	1.8	0.09	27	37*	3.0	4.4	0.4	5.3
$CaCl_2$	M	1.1	1.1	13	0.02	7.2	0.4	15	21	0.7*	1.4*	4.4*	0.15	0.02	0.13	6.8*	3.4*	0.01
	SD	1.6	1	5.2	0.05	1.2	0.3	2.1	22	0.5*	0.8*	3.6*	0.03	0.02	0.07	8.1*	1.5*	0.2
	Min	0.1	0.2	8.6	0	5.7	0	12	8.7	0.2*	0.4*	0.3*	0.10	0.00	0.02	2.6*	0.9*	0.0
	Max	5.2	3.6	23	0.13	8.8	0.8	18	77	1.3*	2.6*	12*	0.20	0.06	0.27	28*	5.7*	0.3
NH_4NO_3	M	0.6	0.7	57	0.1	11	0.6	2.8	21	1.6*	1.1*	4.8*	0.13	0.513*	0.04	5.2*	3.8*	0.001
	SD	0.4	0.4	13	0.3	1.7	0.2	0.9	22	1.1*	0.6*	1.2*	0.04	0.003*	0.02	2.6*	1.4*	0.02
	Min	0.2	0.3	44	0	7.2	0.3	1.7	8.7	1.0*	0.3*	2.9*	0.06	0.511*	0.00	0.7*	1.2*	0.001
	Max	1.3	1.3	83	0.6	12	0.8	4.3	77	4.3*	2.3*	6.3*	0.19	0.517*	0.06	9.4*	6.0*	0.03
Pseudo-total																		
Aqua regia	M	4160	4380	2920	66	220	190	35	295	4.0	13	11	106	1.2	17	29	19	8.2
	SD	686	777	376	12	92	60	19	200	0.3	0.9	0.9	8.2	0.2	5.5	74	1.2	1.4
	MIN	3090	3500	2400	53	92	87	14	15.2	3.6	12	9.0	93	1.0	8.8	0.9	17	6.6
	MAX	5020	5720	3520	82	380	270	68	541	4.3	14	12	118	1.4	23	230	20.54	11

**The values were not taken into consideration because of the type of used Na-salt of complexing extractant solution Na_2EDTA

Table 8.2.2: Descriptive statistics (Mean−M, Standard Deviation−SD) of the element concentrations in the grapevine parts (leaf, seed, pulp and skin) (mg kg^{-1}, **µg kg^{-1}) (n=3) (Experiment 1; Milićević et al., 2017a)

PTEs (major and trace elements)		Al	Cd**	Cr	Cu	Fe	K	Ni	Pb	Zn
Riesling rain seed (*RRSE)	M	< DL	6	0.034	3.6	9.6	1403	0.15	0.032	4.8
	SD	/	0.1	0.001	0.6	1.0	320	0.01	0.002	0.1
Cabernet franc seed (*CSSE)	M	0.9	6	0.16	4.5	11.2	2099	0.080	0.023	5.7
	SD	0.1	0.2	0.02	0.6	1.2	430	0.001	0.002	0.2
Merlot seed (*MSE)	M	0.1	3	0.023	4.1	10.2	1885	0.041	< DL	4.9
	SD	0.0	0.1	0.002	0.3	0.8	470	0.001	/	0.2
Prokupac seed (*PSE)	M	0.3	4	0.027	4.7	9.3	1108	0.050	0.042	3.8
	SD	0.0	0.1	0.001	0.9	1.1	320	0.001	0.006	0.1
Cabernet sauvignon seed (*CSSE)	M	0.4	3	0.038	4.6	11.4	1585	0.119	0.060	4.7
	SD	0.0	0.1	0.001	0.8	1.2	110	0.002	0.008	0.3
Burgundy seed (*BSE)	M	0.6	5	0.083	5.1	14.3	1444	0.102	0.021	5.7
	SD	0.0	0.1	0.001	1.1	1.2	260	0.006	0.002	0.2
Cabernet sauvignon pulp (*CSP)	M	0.6	6	0.420	1.4	5.2	1956	0.075	0.11	0.60
	SD	0.1	0.2	0.008	0.1	0.3	480	0.008	0.01	0.08
Burgundy pulp (*BP)	M	0.5	4	0.14	1.1	5.4	1796	0.050	0.169	0.40
	SD	0.1	0.1	0.01	0.5	0.6	420	0.004	0.009	0.06
Riesling rain skin (*RRS)	M	0.8	5	0.028	1.5	4.8	1237	0.099	0.049	1.3
	SD	0.1	0.1	0.001	0.6	0.6	320	0.007	0.007	0.1
Cabernet franc skin (*CFS)	M	1.7	4	0.007	1.7	5.9	1604	0.050	< DL	1.2
	SD	0.1	0.1	0.001	0.2	0.8	280	0.003	/	0.1
Merlot skin (*MS)	M	0.8	4	0.005	1.2	4.1	1212	0.045	< DL	0.61
	SD	0.1	0.1	0.001	0.1	0.2	630	0.007	/	0.07
Prokupac skin (*PS)	M	4	6	0.045	1.2	7.8	755	52	0.24	1.12
	SD	0.3	0.2	0.001	0.1	0.2	140	3	0.03	0.01
Cabernet sauvignon skin (*CSS)	M	1.1	2	0.22	1.2	5.2	1124	0.12	< DL	0.73
	SD	0.1	0.1	0.01	0.1	0.3	380	0.01	/	0.09
Burgundy skin (*BS)	M	2.3	4	0.093	1.8	6.8	1032	0.09	0.062	1.1
	SD	0.6	0.1	0.003	0.1	0.2	510	0.01	0.008	0.1
Riesling rain skin (*RRS)	M	70	20	0.28	140	100	2585	0.872	0.19	14
	SD	0.8	1.2	0.02	8	8	380	0.006	0.01	0.1
Cabernet franc leaf (*CFL)	M	52	33	0.26	63	72	1913	0.44	0.023	12.0
	SD	5	1.6	0.02	10	10	380	0.01	0.003	2.3
Merlot leaf (*ML)	M	79	20	0.31	29	120	1973	0.72	0.0043	7.8
	SD	11	2.6	0.04	3	20	520	0.06	0.0001	0.8
Prokupac leaf (*PL)	M	72	20	0.30	90	110	1080	0.72	0.365	7.3
	SD	12	2.1	0.01	10	10	180	0.08	0.008	0.8
Cabernet sauvignon leaf (*CSL)	M	60	20	0.29	82	100	2035	0.44	0.072	9
	SD	10	3	0.01	20	20	240	0.03	0.007	1.1
Burgundy leaf (*BL)	M	44	20	0.25	120	110	2588	1.4	0.039	7.6
	SD	8	1.6	0.02	20	20	470	0.2	0.007	0.9
Riesling italian leaf (*RIL)	M	51	20	0.24	170	89	1971	1.03	0.062	11
	SD	7	2.0	0.02	10	10	550	0.09	0.008	1

**µg g^{-1}

Table 8.2.3: CF and PLI calculated for the elements in the soil samples (Experiment 1; Milićević et al., 2017a)

Soil samples	CF Cd	CF Co	CF Cr	CF Cu	CF Fe	CF Mo	CF Ni	CF Pb	CF V	CF Zn	PLI
T1	0.96	1.02	0.89	0.98	1.06	0.83	0.77	0.64	0.94	1.06	0.90
T2	1.03	1.05	0.94	1.06	1.13	0.86	0.57	0.28	0.99	0.97	0.83
T3	0.91	0.93	0.89	0.92	0.81	0.85	0.38	0.10	0.89	0.82	0.65
T4	0.97	0.96	0.92	1.00	0.80	0.92	0.46	0.23	0.95	1.22	0.77
T5	0.99	0.99	1.06	1.01	0.80	0.96	0.60	0.56	0.97	1.30	0.90
T6	0.83	0.88	0.80	0.83	0.69	0.72	0.94	27.3	0.82	0.89	1.16
T10	0.94	0.96	0.93	0.93	0.74	0.81	0.98	0.96	0.91	1.07	0.92
P	0.89	0.87	0.92	0.87	0.77	0.92	0.94	0.43	0.91	0.81	0.82
Soil samples	CF Cd	CF Co	CF Cr	CF Cu	CF Fe	CF Mo	CF Ni	CF Pb	CF V	CF Zn	PLI
T1	0.96	1.02	0.89	0.98	1.06	0.83	0.77	0.64	0.94	1.06	0.90
T2	1.03	1.05	0.94	1.06	1.13	0.86	0.57	0.28	0.99	0.97	0.83
T3	0.91	0.93	0.89	0.92	0.81	0.85	0.38	0.10	0.89	0.82	0.65
T4	0.97	0.96	0.92	1.00	0.80	0.92	0.46	0.23	0.95	1.22	0.77
T5	0.99	0.99	1.06	1.01	0.80	0.96	0.60	0.56	0.97	1.30	0.90
T6	0.83	0.88	0.80	0.83	0.69	0.72	0.94	27.3	0.82	0.89	1.16
T10	0.94	0.96	0.93	0.93	0.74	0.81	0.98	0.96	0.91	1.07	0.92

Table 8.2.4: I_{geo} and EF calculated for the elements in the soil samples (Experiment 1; Milićević et al., 2017a)

I_{geo}										
	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	V	Zn
T1	-0.6	-0.6	-0.7	-0.6	-0.5	-0.9	-1.0	-1.2	-0.7	-0.5
T2	-0.5	-0.5	-0.7	-0.5	-0.4	-0.8	-1.4	-2.4	-0.6	-0.6
T3	-0.7	-0.7	-0.7	-0.7	-0.9	-0.8	-2.0	-3.9	-0.8	-0.9
T4	-0.6	-0.7	-0.7	-0.6	-0.9	-0.7	-1.7	-2.7	-0.7	-0.3
T5	-0.6	-0.6	-0.5	-0.6	-0.9	-0.6	-1.3	-1.4	-0.6	-0.2
T6	-0.9	-0.8	-0.9	-0.8	-1.1	-1.0	-0.7	**4.2**	-0.9	-0.8
T10	-0.7	-0.6	-0.7	-0.7	-1.0	-0.9	-0.6	-0.7	-0.7	-0.5
P	-0.8	-0.8	-0.7	-0.8	-1.0	-0.7	-0.7	-1.8	-0.7	-0.9
EF_{Al}										
	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	V	Zn
T1	1.0	1.1	0.9	1.0	1.1	0.9	0.8	0.7	1.0	1.1
T2	1.0	1.0	0.9	1.0	1.1	0.8	0.6	0.3	1.0	1.0
T3	1.1	1.2	1.1	1.2	1.0	1.1	0.5	0.1	1.1	1.0
T4	1.3	1.3	1.2	1.3	1.1	1.2	0.6	0.3	1.3	**1.6**
T5	1.1	1.1	1.1	1.1	0.9	1.0	0.7	0.6	1.1	1.4
T6	1.3	1.4	1.3	1.3	1.1	1.2	**1.5**	**44**	1.3	1.4
T10	1.3	1.3	1.2	1.3	1.0	1.1	1.3	1.3	1.2	1.4
P	1.2	1.1	1.2	1.1	1.0	1.2	1.2	0.6	1.2	1.1

Table 8.2.5: BAC for Cu, Ni and Zn from soil in different grapevine parts and varieties (Experiment 1; Milićević et al., 2017a)

Grapevine varieties and grapevine parts/soil	Cu	Ni	Zn
BAC factor grapevine parts/T2			
Riesling rain seed (*RRSE)/soil	*	*	*
Burgundac seed (*BSE)/soil	*	*	*
Burgundac pulp (*BP)/soil	*	*	*
Riesling rain skin (*RRS)/soil	*	*	*
Burgundac skin (*BS)/soil	*	*	*
Riesling rain leaf (*RRL)/soil	**1.19**	*	**1.77**
Burgundac leaf (*BL)/soil	**1.02**	*	*
BAC factor grapevine parts/T3			
Cabernet sauvignon seed (*CSSE)/soil	*	*	*
Cabernet sauvignon pulp (*CSP)/soil	*	*	*
Cabernet sauvignon skin (*CSS)/soil	*	*	*
Cabernet sauvignon leaf (*CSL)/soil	*	*	**1.36**
Riesling italian leaf (*RIL)/soil	**1.66**	*	**1.66**
BAC factor grapevine parts/T4			
Prokupac seed (*PSE)/soil	*	*	*
Cabernet sauvignon seed (*CSSE)/soil	*	*	*
Cabernet sauvignon pulp (*CSP)/soil	*	*	*
Prokupac skin (*PS)/soil	*	**4.89**	*
Cabernet sauvignon skin (*CSS)/soil	*	*	*
Prokupac leaf (*PL)/soil	*	*	*
Cabernet sauvignon leaf (*CSL)/soil	*	*	*
BF factor grapevine parts/T6			
Cabernet franc seed (*CSSE)/soil	*	*	*
Cabernet franc skin (*CFS)/soil	*	*	*
Cabernet franc leaf (*CFL)/soil	*	*	**1.66**
BF factor grapevine parts/T10			
Cabernet franc seed (*CSSE)/soil	*	*	*
Merlot seed (*MSE)/soil	*	*	*
Cabernet franc skin (*CFS)/soil	*	*	*
Merlot skin (*MS)/soil	*	*	*
Cabernet franc leaf (*CFL)/soil	*	*	**1.38**
Merlot leaf (*ML)/soil	*	*	*
BAC factor grapevine parts/P			
Cabernet franc seed (*CSSE)/soil	*	*	*
Cabernet franc skin (*CFS)/soil	*	*	*
Cabernet franc leaf (*CFL)/soil	*	*	**1.82**

*calculated values lower than 1

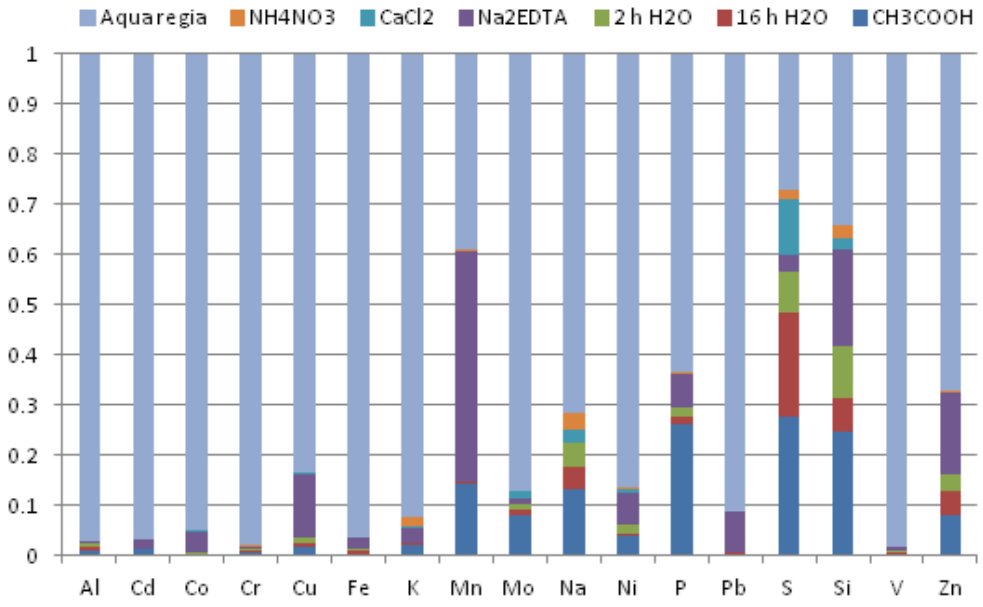


Figure 8.2.1 Overview of extracted major and trace elements according to the pseudo-total digestion.

8.3 Appendix 3: Experiment 2

Table 8.3.1 Descriptive statistics (Median−M, Minimum, Maximum, Median of Percentage − MF% single extraction vs. pseudo-total) of the single-extracted and pseudo-total element concentrations (mg kg^{-1}) from the topsoil (0–30 cm) and subsoil (30–60 cm) samples (Experiment 2; Milićević et al., 2018a)

		Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
Deionised water 2 h																							
0–30 cm	M	9.9	<DL	0.009	0.60	0.0034	150	0.0011	0.0065	0.022	0.63	2.72	6.07	0.0033	11	0.29	7.0	0.05	0.046	<DL	0.24	0.014	0.493
	Min	1.2	<DL	0.005	0.29	0.0017	44	0.0007	0.0011	0.003	0.11	0.27	1.38	0.0004	6	0.12	4.1	0.01	0.004	<DL	0.12	0.007	0.001
	Max	110.8	<DL	3.368	2.49	0.0110	256	0.0098	0.0217	0.334	1.23	72.76	18.10	0.0531	32	0.71	21.9	0.43	1.355	<DL	0.52	0.134	2.124
	MF%	0.016	/	0.021	0.235	0.188	1.67	0.029	0.025	0.016	1.450	0.007	0.013	0.00001	0.132	0.027	0.906	0.050	0.252	/	0.589	0.024	0.444
30–60 cm	M	19.4	<DL	0.009	0.88	0.0053	142	0.0015	0.0098	0.034	0.73	4.65	3.71	0.0045	12	0.31	9.1	0.07	0.086	<DL	0.26	0.016	0.860
	Min	4.1	<DL	0.002	0.26	0.0013	49	0.0007	0.0023	0.017	0.32	1.33	1.30	0.0002	4	0.18	4.4	0.03	0.004	<DL	0.09	0.006	0.235
	Max	65.3	<DL	20.726	3.24	0.0152	248	0.0080	0.0239	0.220	3.83	39.01	9.25	0.0316	25	1.19	69.3	1.29	0.544	<DL	0.39	0.079	6.839
	MF%	0.029	/	0.022	0.323	0.245	1.809	0.116	0.038	0.023	1.618	0.011	0.039	0.0001	0.151	0.029	1.104	0.052	0.314	/	0.550	0.018	1.038
Deionised water 16 h																							
0–30 cm	M	10.3	<DL	0.020	0.27	0.0003	48	0.0015	0.0267	0.040	0.47	4.30	3.68	0.0090	17	0.25	2.7	0.10	0.067	<DL	0.14	0.004	0.129
	Min	0.8	<DL	0.005	0.08	0.0003	7	0.0007	0.0030	0.013	0.06	1.33	0.46	0.0014	7	0.03	1.9	0.01	0.012	<DL	0.05	0.004	0.001
	Max	46.1	<DL	3.611	1.80	0.0078	196	0.0027	0.0735	0.272	1.13	43.5	9.53	0.0566	44	0.71	35.6	5.14	0.189	<DL	0.38	0.043	1.274
	MF%	0.014	/	0.034	0.102	0.014	0.51	0.037	0.103	0.028	1.021	0.009	0.085	0.0002	0.214	0.024	0.376	0.096	0.390	/	0.323	0.006	0.189
30–60 cm	M	15.4	<DL	0.059	0.40	0.0003	36	0.0015	0.0279	0.067	0.44	9.60	2.00	0.0127	12	0.20	3.0	0.09	0.067	<DL	0.10	0.004	0.150
	Min	1.0	<DL	0.001	0.07	0.0003	6	0.0001	0.0031	0.004	0.06	0.78	0.22	0.0008	5	0.06	2.0	0.01	0.001	<DL	0.04	0.004	0.001
	Max	49.4	<DL	10.357	2.76	0.0026	61	0.0052	0.0702	0.224	3.05	38.0	12.9	0.0542	44	1.30	41.2	1.03	0.183	<DL	0.26	0.044	1.828
	MF%	0.018	/	0.147	0.150	0.012	0.49	0.117	0.102	0.037	1.267	0.019	0.021	0.0003	0.140	0.020	0.404	0.070	0.282	/	0.225	0.004	0.161
$CaCl_2$																							
0–30 cm	M	1.7	<DL	0.006	1.44	0.0009	/	0.0027	0.0022	0.006	0.105	1.58	33	0.0098	183	0.25	9.0	0.030	<DL	<DL	2.87	0.007	0.002
	Min	0.8	<DL	0.006	0.77	0.0002	/	0.0011	0.0009	0.001	0.005	0.74	9	0.0004	59	0.01	3.9	0.003	<DL	<DL	1.25	0.003	0.002
	Max	3.2	<DL	4.682	4.26	0.0025	/	0.0123	0.0335	0.011	3.042	2.46	61	0.0292	337	12.79	36.4	0.962	<DL	<DL	3.89	0.014	0.335
	MF%	0.002	/	0.014	0.688	0.049	/	0.079	0.009	0.004	0.300	0.004	0.24	0.0002	2.158	0.060	1.233	0.041	/	/	6.87	0.009	0.002
30–60 cm	M	2.0	<DL	0.006	1.40	0.0007	/	0.0022	0.0026	0.006	0.051	1.64	17	0.0098	196	0.22	13.1	0.021	<DL	<DL	2.90	0.006	0.002
	Min	1.0	<DL	0.006	0.77	0.0002	/	0.0011	0.0009	0.001	0.001	0.86	7	0.0017	44	0.01	5.6	0.003	<DL	<DL	1.43	0.003	0.002
	Max	4.7	<DL	24.681	5.49	0.0078	/	0.0205	0.1136	0.086	0.585	4.08	47	0.0373	357	26.07	110.0	1.614	<DL	<DL	4.11	0.011	0.643
	MF%	0.003	/	0.015	0.577	0.032	/	0.224	0.012	0.004	0.135	0.004	0.19	0.0002	2.653	0.029	1.750	0.022	/	/	6.17	0.007	0.002

	NH_4NO_3																					
0–30 cm	M	2.0	<DL	0.003	33.1	0.0013	3060	<DL	0.0020	0.005	0.041	1.63	129	0.07	246	0.47	8.9	0.044	<DL	<DL	5.95	0.007	0.030
	Min	0.5	<DL	0.003	20.0	0.0002	2029	<DL	0.0001	0.000	0.005	0.58	74	0.05	67	0.05	5.2	0.003	<DL	<DL	3.80	0.002	0.001
	Max	6.1	<DL	0.439	66.9	0.0078	3902	<DL	0.0408	0.013	4.151	3.66	225	0.09	558	21.21	30.9	1.713	<DL	<DL	7.82	0.013	0.434
	MF%	0.003	/	0.007	14.181	0.061	36.044	/	0.007	0.003	0.095	0.004	0.319	0.002	3.125	0.099	1.208	0.048	/		14.005	0.009	0.063
30–60 cm	M	2.5	<DL	0.003	38.6	0.0013	3246	<DL	0.0018	0.006	0.069	1.66	94	0.07	295	0.47	13.5	0.039	<DL	<DL	6.35	0.006	0.037
	Min	0.0	<DL	0.003	21.3	0.0002	1960	<DL	0.0001	0.001	0.002	0.43	68	0.05	57	0.05	5.4	0.004	<DL	<DL	4.37	0.003	0.001
	Max	24.7	<DL	7.714	56.5	0.0342	4513	<DL	0.1432	0.017	43.849	4.42	163	0.10	553	33.31	86.3	2.475	<DL	<DL	9.12	0.012	0.800
	MF%	0.004	/	0.008	13.655	0.060	42.078	/	0.007	0.004	0.175	0.004	0.969	0.001	3.750	0.060	1.772	0.035	/		13.3	0.006	0.055
	Na_2EDTA																					
0–30 cm	M.	324	0.17	<DL	13.6	0.0017	4283	0.08	6.20	0.005	6.7	178	41	0.08	186	352	/	8.03	7.90	<DL	5.07	1.357	2.890
	Min	54	0.00	<DL	4.1	0.0004	1924	0.04	1.40	0.005	4.2	62	13	0.07	73	189	/	2.94	3.54	<DL	3.33	0.544	1.141
	Max	463	0.37	<DL	20.1	0.0302	18945	0.23	7.98	0.039	25.7	284	74	0.10	324	484	/	13.66	10.8	<DL	19.61	2.630	6.270
	MF%	0.450	0.01	0.040	5.61	0.126	47.9	1.96	23.3	0.004	15.133	0.424	0.946	0.002	2.321	32.331	/	7.843	44.4	/	11.43	1.783	2.851
30–60 cm	M	306	0.09	<DL	13.5	0.0049	3257	0.06	5.62	0.005	5.2	154	19	0.08	183	292	/	6.12	6.49	<DL	4.64	1.112	1.395
	Min	28	0.01	<DL	4.0	0.0000	1573	0.01	0.24	0.004	1.4	26	7	0.05	58	47	/	1.34	2.14	<DL	1.83	0.129	0.501
	Max	561	0.31	<DL	21.2	0.0346	19247	0.14	8.82	0.750	394.2	334	63	0.11	333	538	/	13.59	11.3	<DL	21.6	2.507	8.065
	MF%	0.450	0.006	0.043	5.09	0.199	44.2	4.68	22.4	0.003	14.557	0.393	0.197	0.002	2.329	26.409	/	5.082	27.4	/	9.12	1.017	1.414
	CH_3COOH																					
0–30 cm	M	44	<DL	0.10	21.1	0.15	1512	0.0113	0.27	0.085	0.010	11	96	0.19	310	38	15.9	8.94	0.04	<DL	5.63	0.025	0.778
	Min	20	<DL	0.01	14.6	0.02	762	0.0022	0.03	0.039	0.010	6	43	0.10	156	22	11.3	6.92	0.01	<DL	4.11	0.009	0.130
	Max	54	<DL	9.17	26.3	0.21	36400	0.0519	0.43	0.150	192.6	15	208	0.82	421	111	43.5	22.69	0.25	<DL	54.9	0.046	3.029
	MF%	0.062	/	0.141	8.400	7.900	16.798	0.290	1.093	0.056	0.024	0.027	0.819	0.005	3.59	3.427	2.103	8.562	0.219	/	13.2	0.036	1.028
30–60 cm	M.	38	<DL	0.10	21.5	0.16	1253	0.0095	0.23	0.084	0.010	11	62	0.19	295	31	21.8	12.14	0.04	<DL	5.73	0.024	0.319
	Min	15	<DL	0.05	12.3	0.00	717	0.0006	0.02	0.035	0.003	5	33	0.08	121	17	14.1	7.72	0.03	<DL	3.62	0.002	0.002
	Max	58	<DL	36.00	27.1	0.21	64455	0.0449	0.50	0.878	6.885	16	114	1.33	463	175	125.6	63.39	0.11	<DL	76.1	0.046	3.820
	MF%	0.056	/	0.250	7.286	7.740	16.373	0.764	1.043	0.052	0.027	0.024	0.657	0.004	3.66	3.171	2.850	9.319	0.151	/	11.9	0.023	0.780
	Pseudo-total																					
0–30 cm	M	71351	13.9	41.9	255	1.97	8561	3.90	25.8	142	43.2	42381	11516	40.2	9214	1083	750	108	16.9	3.19	42.4	65.8	82.3
	Min	60784	8.6	33.7	210	1.70	5342	3.56	21.3	94	38.1	40138	10304	35.7	7731	904	699	62	13.0	2.62	28.5	56.0	71.5
	Max	81568	17.6	59.8	284	2.41	60997	4.40	33.6	221	82.9	47782	13121	43.4	12152	1681	866	199	27.7	4.22	95.6	71.7	101.1
	C	69945	15.4	19.7	331	1.92	6696	0.28	16.5	87	51.6	40977	11268	38.0	8280	1122	817	59	28.4	5.30	104.3	105.8	85.3
30–60 cm	M	69049	15.6	41.4	293	2.09	8001	1.26	25.7	153	39.3	43681	9873	47.8	9397	1075	772	134	22.6	5.22	48.2	94.7	82.9
	Min	8536	1.2	11.0	129	0.16	4764	0.44	17.4	34	26.9	10236	1634	8.6	6390	767	395	33	6.9	1.57	33.6	0.9	55.8
	Max	81384	19.0	96.3	424	2.84	96473	2.37	31.2	257	90.2	52079	13715	58.9	12629	1755	1000	298	54.4	6.89	147.7	107.7	131.2
	C	69795	12.9	43.7	275	2.02	6329	2.17	21.3	78	112.5	44013	9592	38.0	8960	882	456	51	17.3	2.46	47.1	64.6	89.1
	MAC		25	50	/	/	/	3	/	100	100	/	/	/	/	/	/	50	100	/	/	/	300

M – Median; DL – detection limit MAC – maximum allowed concentrations (Official Gazette of Republic of Serbia); C – control sample

Table 8.3.2 Spearman's correlation coefficients between the element concentrations within different soil layers – topsoil and subsoil (Experiment 2; Milićević et al., 2018a)

Spearman's R between elements in soil (0-30 cm)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
Al	1.00																					
As	-0.55	1.00																				
B	0.09	-0.02	1.00																			
Ba	0.36	-0.30	-0.63	1.00																		
Be	0.39	-0.02	-0.63	0.84	1.00																	
Ca	-0.22	0.47	0.26	-0.58	-0.37	1.00																
Cd	0.24	0.13	-0.53	0.65	0.84	-0.21	1.00															
Co	0.18	-0.30	0.29	0.25	0.09	-0.29	0.19	1.00														
Cr	0.16	0.04	0.55	-0.52	-0.36	0.57	-0.12	0.17	1.00													
Cu	0.04	-0.09	0.21	-0.24	-0.32	0.19	-0.01	0.16	0.30	1.00												
Fe	0.66	-0.18	-0.17	0.35	0.58	-0.13	0.74	0.15	0.23	0.15	1.00											
K	0.40	0.20	0.66	-0.40	-0.16	0.33	-0.07	0.01	0.63	0.05	0.32	1.00										
Li	0.42	0.24	0.10	0.05	0.31	0.40	0.29	-0.33	0.36	-0.24	0.47	0.61	1.00									
Mg	0.36	-0.01	0.59	-0.60	-0.44	0.58	-0.27	0.01	0.82	0.39	0.21	0.71	0.34	1.00								
Mn	-0.27	-0.23	-0.25	0.46	0.07	-0.33	0.07	0.47	-0.41	0.17	-0.21	-0.61	-0.53	-0.53	1.00							
Na	-0.03	-0.08	-0.32	0.39	0.30	-0.18	0.32	0.13	-0.07	-0.15	0.02	-0.26	-0.09	-0.25	0.08	1.00						
Ni	0.11	0.07	0.53	-0.46	-0.34	0.63	-0.09	0.23	0.94	0.34	0.18	0.61	0.36	0.79	-0.28	-0.11	1.00					
Pb	-0.39	0.32	0.02	-0.01	-0.16	-0.10	-0.28	0.12	-0.39	0.04	-0.59	-0.27	-0.53	-0.33	0.31	-0.09	-0.35	1.00				
Sb	0.22	0.20	0.54	-0.57	-0.29	0.52	-0.15	-0.07	0.67	0.15	0.24	0.77	0.48	0.78	-0.58	-0.43	0.69	-0.28	1.00			
Sr	-0.56	0.27	0.54	0.21	0.18	0.06	0.32	-0.20	-0.28	0.05	-0.14	-0.55	-0.23	-0.46	0.41	0.32	-0.23	0.00	-0.49	1.00		
V	0.85	-0.72	-0.13	0.54	0.46	-0.44	0.31	0.31	-0.02	0.01	0.55	-0.02	0.13	0.09	-0.02	0.23	-0.11	-0.38	-0.14	-0.33	1.00	
Zn	0.20	0.25	0.09	0.13	0.18	0.02	0.34	0.16	0.18	0.16	0.22	0.35	0.14	0.15	-0.17	0.28	0.18	0.25	0.22	-0.05	0.05	1.00

Spearman's R between elements in soil (30-60 cm)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
Al	1.00																					
As	0.31	1.00																				
B	0.30	0.05	1.00																			
Ba	0.40	0.37	-0.13	1.00																		
Be	0.35	0.46	-0.33	0.80	1.00																	
Ca	-0.08	-0.14	-0.02	0.53	-0.40	1.00																
Cd	0.25	0.64	-0.02	0.12	0.17	0.09	1.00															
Co	0.22	0.48	0.06	0.41	0.32	-0.63	0.48	1.00														
Cr	0.44	0.04	0.47	-0.11	0.00	0.41	0.19	-0.09	1.00													
Cu	0.32	0.36	0.30	0.01	-0.01	-0.03	0.51	0.20	0.13	1.00												
Fe	0.66	0.67	0.02	0.34	0.49	0.01	0.76	0.47	0.39	0.39	1.00											
K	0.66	0.10	0.62	-0.19	-0.21	0.39	0.17	-0.20	0.74	0.38	0.35	1.00										
Li	0.76	0.38	0.00	0.73	0.79	-0.27	0.10	0.26	0.32	0.10	0.60	0.24	1.00									
Mg	0.68	-0.07	0.55	-0.15	-0.17	0.32	0.11	-0.09	0.78	0.30	0.35	0.88	0.32	1.00								
Mn	-0.28	0.22	0.01	0.49	0.12	-0.53	0.06	0.42	-0.34	-0.03	-0.12	-0.47	-0.04	-0.53	1.00							
Na	0.44	0.05	0.40	-0.16	-0.24	0.44	0.09	-0.21	0.63	0.35	0.21	0.80	0.16	0.78	-0.25	1.00						
Ni	0.23	-0.13	0.34	-0.22	-0.07	0.44	0.20	-0.07	0.90	0.03	0.24	0.56	0.12	0.66	-0.40	0.46	1.00					
Pb	-0.20	0.26	-0.11	0.57	0.41	-0.62	-0.24	0.25	0.43	-0.07	-0.26	-0.51	0.19	-0.49	0.66	-0.30	-0.50	1.00				
Sb	0.49	0.23	0.42	-0.18	-0.04	0.47	0.44	-0.06	0.87	0.36	0.58	0.76	0.28	0.76	-0.40	0.62	0.75	-0.60	1.00			
Sr	-0.62	-0.11	0.45	-0.10	-0.07	0.33	-0.18	-0.41	-0.33	-0.17	-0.34	-0.35	-0.39	-0.47	0.18	-0.10	-0.28	0.08	-0.28	1.00		
V	0.63	0.20	-0.02	0.83	0.76	-0.46	-0.05	0.34	0.19	0.03	0.40	0.07	0.88	0.22	0.12	0.07	0.05	0.36	0.02	-0.36	1.00	
Zn	0.37	0.70	-0.17	0.46	0.66	-0.24	0.51	0.30	0.04	0.48	0.59	0.04	0.52	0.04	-0.07	0.00	-0.07	0.26	0.19	-0.11	0.41	1.00

$p<0.01$
$p<0.05$

Table 8.3.3 Descriptive statistics (Median, Minimum, Maximum, Mean and Standard Deviation) of the element concentrations (mg kg^{-1}) in the grapevine parts (leaf, skin, pulp, and seed) and wine (*mg L^{-1}) (Experiment 2; Milićević et al., 2018a)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
Seed																						
M	0.78	0.0019	5.8	26.0	< DL	40722	0.00094	0.00385	0.0218	7.3	15.4	23731	< DL	7645	6.82	44.7	0.076	0.0005	0.00167	3.84	0.00078	7.14
Min	0.10	0.0004	4.2	7.0	< DL	26628	0.00019	0.00012	0.0108	4.0	3.3	21238	< DL	977	0.48	13.2	0.005	0.0005	0.00006	0.77	0.00004	0.34
Max	7.44	0.0073	7.6	58.3	< DL	53893	0.00974	0.01966	0.3322	14.5	20.1	38603	< DL	8844	21.03	466.0	0.549	1.4156	0.01644	8.13	0.02186	10.93
Pulp																						
M	0.79	0.0004	2.5	1.5	< DL	2003	0.00014	0.00006	0.0057	0.8	2.8	11432	< DL	704	0.26	33.1	0.014	0.0003	0.00081	0.30	0.00125	3.00
Min	0.28	0.0001	1.3	0.4	< DL	1117	0.00004	0.00005	0.0045	0.3	1.2	8378	< DL	549	0.15	0.5	0.002	0.0002	0.00003	0.08	0.00003	1.68
Max	6.31	0.0024	5.0	3.4	< DL	3636	0.00409	0.05530	2.4625	25.9	12.0	18840	< DL	966	2.25	59.7	0.111	0.5618	0.00332	1.79	0.00451	6.79
Skin																						
M	0.55	0.0002	6.9	3.9	< DL	3512	0.00025	0.00116	0.0075	1.1	5.2	25923	< DL	1090	0.81	12.8	0.045	0.0003	0.00086	0.89	0.00097	2.00
Min	0.27	0.0000	0.0	1.8	< DL	2371	0.00004	0.00003	0.0043	0.8	4.1	14757	< DL	919	0.44	0.0	0.003	0.0002	0.00001	0.41	0.00003	1.13
Max	10.83	0.0033	9.7	8.9	< DL	4643	0.30453	0.41281	0.0811	7.5	9.0	31568	< DL	1225	3.33	22.7	0.098	0.7741	0.01811	1.56	0.00911	4.60
whole berry																						
M	0.32	0.0002	4.4	3.3	< DL	3882	0.00030	0.00014	0.0050	1.3	3.7	16687	< DL	1209	0.90	21.6	0.032	0.0002	0.00053	0.58	0.00023	0.70
Min	0.17	0.0001	2.3	1.1	< DL	2012	0.00003	0.00005	0.0039	0.8	2.4	12001	< DL	840	0.48	4.3	0.008	0.0002	0.00002	0.24	0.00002	0.19
Max	6.93	0.0022	6.2	8.9	< DL	5862	0.00377	0.00447	0.0092	8.8	8.3	22317	< DL	1562	3.26	34.6	0.203	0.0003	0.00873	1.20	0.00214	1.12
MAC (ff)		0.1					0.05											1				
Leaf																						
M	55	0.08	20	15.9	0.0025	30461	0.0019	0.07	0.20	4.4	107	6477	0.25	2896	56	53	1.14	0.20	0.0106	44	0.10	16
Min	22	0.03	14	7.41	0.0003	25411	0.0004	0.03	0.05	3.2	56	4587	0.09	1954	27	5	0.02	0.01	0.0003	18	0.04	11
Max	98	0.31	48	37.2	0.0192	39573	0.0108	0.25	2.83	6.4	251	9238	0.36	4958	185	120	5.38	2.43	0.4410	64	0.22	29
Sauvignon blanc (wite wine)																						
*Mean	18	0.0017	19.7	0.09	< DL	63	0.002	1.29E-04	0.00028	< DL	33	313	< DL	85.5	0.84	9.3	< DL	< DL	0.02	2.11	0.003	9.3
SD	3	0.0002	0.3	0.04	< DL	1	0.001	0.0000005	1.07E-06	< DL	10	1	< DL	0.2	0.02	0.4	< DL	< DL	0.01	0.03	0.001	0.8
Cabernet sauvignon (red wine)																						
*Mean	10	0.0002	42	0.074	< DL	68	0.002	0.005	0.03	< DL	25	626	< DL	97	1.11	20	0.7	0.086	0.002	2.86	0.0014	6
SD	8	0.0001	1	0.006	< DL	3	0.001	0.003	0.01	< DL	15	11	< DL	2	0.02	2	0.5	0.006	0.001	0.06	0.0007	0.5
*MAC (RS)		0.2					0.1			3.0	5							0.3				5
*MAC (A)		0.1					0.05			5.0								0.2				5
*MAC (G)	8	0.1					0.01			5.0								0.3				5
*MAC (I)										10								0.3				5
*MAC (OIV)		0.2	80				0.01			1.0						60		0.2				5
*MAC (C) 5 wv	10	0.2	80				0.01		0.1	1.0	10					20	0.1	0.3				5
*MAC (C) 5 rv	10	0.2	80				0.01		0.1	1.0	20					20	0.1	0.3				5
*MAC (C) 16 wv							0.01			1.0	10							0.2				5
*MAC (C) 16 rv							0.01			1.0	20							0.2				5

M. – Median; DL– detection limit; MAC – maximum allowed concentrations prescribed by national and international gazettes: MAC(ff) – Officiall Gazette of Republic of Serbia. prescribed values for fresh fruit; Values prescribed for the wine: *MAC (RS) – Republic of Serbia; *MAC (A) – Australia; *MAC (G) – Germany; *MAC (I)-Italy; *MAC (OIV) – International Organisation of Vine and Wine; *MAC (C) 5 wv and *MAC (C) 16 wv – Croatian National Gazettes for wite wine; *MAC (C) 5 rv and *MAC (C) 16 rv – Croatian National Gazettes for red wine.

Table 8.3.4 Spearman's correlation coefficients between the elements in the soil and the grapevine parts (leaf, skin, pulp and seed) (Experiment 2; Milićević et al., 2018a)

Topsoil layer (0–30 cm)–grapevine parts										
soil–leaf	R	*p*	*soil–skin*	R	*p*	*soil–pulp*	R	*p*	*soil–seed*	R	*p*
Ba 2h H_2O–Ba leaf	0.70	*<0.01*	Ba 2h H_2O–Ba skin	0.73	*<0.01*	Ba 2h H_2O–Ba pulp	0.80	*<0.01*	Ba 2h H_2O–Ba seed	0.82	*<0.01*
Ba 16h H_2O–Ba leaf	0.60	*<0.01*	Ba 16h H_2O–Ba skin	0.86	*<0.01*	Ba 16h H_2O–Ba pulp	0.77	*<0.01*	Ba 16h H_2O–Ba seed	0.89	*<0.01*
Ba $CaCl_2$–Ba leaf	0.60	*<0.01*	Ba $CaCl_2$–Ba skin	0.90	*<0.01*	Ba $CaCl_2$–Ba pulp	0.91	*<0.01*	Ba $CaCl_2$–Ba seed	0.95	*<0.01*
Ba NH_4NO_3–Ba leaf	0.68	*<0.01*	Ba NH_4NO_3–Ba skin	0.66	*<0.01*	Ba NH_4NO_3–Ba pulp	0.66	*<0.01*	Ba NH_4NO_3–Ba seed	0.75	*<0.01*
Ba Na_2EDTA–Ba leaf	0.57	*<0.01*	Ba Na_2EDTA–Ba skin	0.53	*<0.01*	Ba Na_2EDTA–Ba pulp	0.51	*<0.01*	Ba Na_2EDTA–Ba seed	0.54	*<0.01*
Ba CH_3COOH–Ba leaf	0.75	*<0.01*	Ba CH_3COOH–Ba skin	0.53	*<0.01*	Sr 2h H_2O–Sr pulp	0.57	*<0.01*	Cr 2h H_2O–Ni seed	0.52	*<0.01*
Ni $CaCl_2$–Ni leaf	0.53	*<0.01*	Sr $CaCl_2$–Sr skin	0.82	*<0.01*	Sr 16h H_2O–Srpulp	0.65	*<0.01*	Cu 2h H_2O–Ni seed	0.56	*<0.01*
Cu Na_2EDTA–Cu leaf	0.56	*<0.01*	Sr 2h H_2O–Sr skin	0.50	*<0.01*	Ba CH_3COOH–Ba pulp	0.43	*<0.05*	Ni 2h H_2O–Ni seed	0.55	*<0.01*
Mn $CaCl_2$–Mn leaf	0.42	*<0.05*	Fe 16h H_2O–Fe skin	0.56	*<0.01*	Sr $CaCl_2$–Sr pulp	0.40	*<0.05*	Ba CH_3COOH–Ba seed	0.49	*<0.05*
Mn NH_4NO_3–Mn leaf	0.47	*<0.05*	V 16h H_2O–V skin	0.44	*<0.01*	Sr Na_2EDTA–Sr pulp	0.40	*<0.05*			
Ni NH_4NO_3–Ni leaf	0.45	*<0.05*	Cu Na_2EDTA–Cu skin	0.40	*<0.05*						
Be NH_4NO_3–Be leaf	0.50	*<0.05*	Zn Na_2EDTA–Zn skin	0.44	*<0.05*						
V Na_2EDTA– V leaf	0.41	*<0.05*	Ni $CaCl_2$–Ni skin	0.40	*<0.05*						
			Sr NH_4NO_3–Sr skin	0.46	*<0.05*						
			Mn NH_4NO_3–Mn skin	0.41	*<0.05*						
Subsoil layer (30–60 cm)–grapevine parts										
soil–leaf	R	*p*	*soil–skin*	R	*p*	*soil–pulp*	R	*p*	*soil–seed*	R	*p*
Ba 2h H_2O–Ba leaf	0.58	*<0.01*	Ba 2h H_2O–Ba skin	0.66	*<0.01*	Ba 2h H_2O–Ba pulp	0.82	*<0.01*	Ba 2h H_2O–Ba seed	0.76	*<0.01*
Ba 16h H_2O–Ba leaf	0.61	*<0.01*	Ba 16h H_2O–Ba skin	0.82	*<0.01*	Ba 16h H_2O–Ba pulp	0.80	*<0.01*	Ba 16h H_2O–Ba seed	0.81	*<0.01*
Ba $CaCl_2$–Ba leaf	0.58	*<0.01*	Ba $CaCl_2$–Ba skin	0.91	*<0.01*	Ba $CaCl_2$–Ba pulp	0.91	*<0.01*	Ba $CaCl_2$–Ba seed	0.96	*<0.01*
Ba NH_4NO_3–Ba leaf	0.57	*<0.01*	Ba NH_4NO_3–Ba skin	0.77	*<0.01*	Ba NH_4NO_3–Ba pulp	0.70	*<0.01*	Ba NH_4NO_3–Ba seed	0.77	*<0.01*
Ba Na_2EDTA–Ba leaf	0.70	*<0.01*	Ba Na_2EDTA–Ba skin	0.73	*<0.01*	Ba Na_2EDTA–Ba pulp	0.65	*<0.01*	Ba Na_2EDTA–Ba seed	0.68	*<0.01*
Ba CH_3COOH–Ba leaf	0.62	*<0.01*	Ba CH_3COOH–Ba skin	0.60	*<0.01*	Ba CH_3COOH–Ba pulp	0.51	*<0.01*	Ba CH_3COOH–Ba seed	0.52	*<0.01*
Sr 16h H_2O–Sr leaf	0.52	*<0.01*	Sr $CaCl_2$–Sr skin	0.78	*<0.01*	Sr 2h H2O–Sr pulp	0.52	*<0.01*	Ni CaCl2–Ni seed	0.62	*<0.01*
Ni $CaCl_2$–Ni leaf	0.50	*<0.05*	Sr NH_4NO_3–Sr skin	0.61	*<0.01*	Sr 16h H2O–Sr pulp	0.51	*<0.01*	Ni NH_4NO_3–Ni seed	0.60	*<0.01*
Ni NH_4NO_3–Ni leaf	0.43	*<0.05*	Al Na_2EDTA–Al skin	0.51	*<0.01*	Sr CaCl2–Sr pulp	0.64	*<0.01*	Sr CaCl2–Sr seed	0.41	*<0.05*
V $CaCl_2$–V leaf	0.44	*<0.05*	Ni $CaCl_2$–Ni skin	0.50	*<0.05*	Sr NH4NO3–Sr pulp	0.58	*<0.01*	Ni 2h H_2O–Ni seed	0.4	*<0.05*
			Ni NH_4NO_3–Ni skin	0.44	*<0.05*	Sr Na2EDTA–Sr pulp	0.56	*<0.01*	Ni 16h H_2O–Ni seed	0.41	*<0.05*
						Al 16h H_2O–Al pulp	0.42	*<0.05*			
						Cu 16h H_2O–Cu pulp	0.44	*<0.05*			
						V 16h H_2O–V pulp	0.40	*<0.05*			
						V Na_2EDTA–V pulp	0.44	*<0.05*			

Table 8.3.5 CF calculated for the potentially toxic elements measured in the vineyard soil samples (Experiment 2; Milićević et al., 2018a)

	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
Sample	CF (0−30 cm)																	
1	0.99	0.95	2.12	0.79	1.05	13.94	1.63	1.60	1.09	1.04	1.19	0.99	1.75	0.89	0.49	0.45	0.62	0.97
2	0.95	0.90	2.05	0.79	1.01	13.31	1.55	1.37	1.19	1.00	1.25	0.92	1.57	0.79	0.53	0.43	0.60	0.96
3	0.94	0.88	2.05	0.80	1.01	13.50	1.70	1.43	0.78	1.00	1.38	0.88	1.72	0.75	0.54	0.40	0.61	0.88
4	1.00	0.89	1.84	0.80	1.07	13.79	1.58	1.48	0.76	1.03	1.09	0.95	1.74	0.61	0.57	0.41	0.63	0.92
5	1.06	0.88	1.77	0.81	1.11	14.27	1.44	1.30	1.61	1.07	0.97	0.90	1.39	0.54	0.59	0.41	0.65	0.95
6	1.06	0.86	1.71	0.83	1.12	13.82	1.29	1.08	0.75	1.04	0.90	0.92	1.06	0.55	0.57	0.42	0.64	0.94
7	1.13	0.91	1.77	0.83	1.26	14.45	1.50	1.33	0.80	1.09	0.87	0.98	1.57	0.53	0.56	0.40	0.68	0.95
8	1.06	0.87	1.98	0.83	1.16	14.12	1.54	1.81	0.83	1.06	0.97	0.91	2.68	0.56	0.67	0.41	0.63	0.97
9	1.12	0.89	2.12	0.84	1.15	15.47	1.99	2.33	0.85	1.17	1.00	1.05	3.41	0.46	0.70	0.41	0.68	1.06
10	0.91	1.14	1.91	0.72	0.97	13.25	1.42	1.66	0.83	0.98	0.90	1.00	1.86	0.81	0.60	0.57	0.57	1.07
11	0.98	0.93	2.07	0.77	1.06	13.84	1.64	1.53	0.81	1.02	1.05	1.00	1.77	0.67	0.60	0.46	0.62	1.03
12	0.95	0.91	2.32	0.81	1.01	14.06	2.04	1.42	1.04	1.00	1.50	1.03	1.82	0.98	0.55	0.43	0.60	1.19
13	1.02	0.83	2.35	0.82	1.08	13.51	1.68	1.35	0.74	1.02	1.08	1.00	1.40	0.55	0.54	0.42	0.64	0.89
14	1.10	0.87	2.03	0.86	1.11	14.46	1.56	1.52	0.81	1.10	1.06	1.02	1.61	0.50	0.54	0.45	0.65	1.15
15	1.07	0.67	2.57	0.67	0.91	13.48	1.63	2.54	0.93	1.06	0.86	0.91	2.90	0.51	0.80	0.32	0.64	1.03
16	1.15	0.78	2.66	0.71	0.90	12.63	1.59	1.74	0.93	1.03	0.91	0.86	1.95	0.66	0.71	0.31	0.65	0.97
17	1.17	0.56	2.97	0.77	0.91	12.51	1.74	1.66	0.91	1.02	1.28	0.89	2.17	0.63	0.60	0.32	0.65	0.92
18	1.02	0.78	2.60	0.66	0.89	12.74	1.52	1.94	0.84	1.03	0.81	1.06	2.13	0.52	0.61	0.27	0.64	0.94
19	0.99	1.03	2.45	0.73	1.01	13.24	1.43	1.57	0.81	0.98	0.90	0.91	1.81	0.72	0.69	0.38	0.59	0.96
20	1.02	0.97	3.04	0.73	1.04	13.75	1.56	1.74	0.81	1.03	0.83	0.90	2.04	0.65	0.64	0.39	0.61	1.11
21	1.02	0.98	2.14	0.74	1.09	14.49	1.63	2.01	0.87	1.08	0.89	0.91	2.33	0.53	0.67	0.41	0.61	0.95
22	0.87	0.93	2.12	0.65	0.90	13.12	1.44	1.88	0.85	0.99	0.97	0.93	2.28	0.49	0.57	0.89	0.54	0.84
23	1.00	1.01	2.36	0.73	1.00	13.06	1.49	1.51	0.81	1.00	0.96	0.90	1.76	0.73	0.67	0.38	0.59	0.97
24	1.02	0.98	2.46	0.70	1.02	13.67	1.57	1.68	0.83	1.06	0.85	0.90	1.99	0.63	0.75	0.35	0.59	1.02
25	1.05	0.97	2.26	0.73	1.06	14.23	1.62	1.69	0.88	1.10	0.94	0.91	2.12	0.58	0.72	0.37	0.60	1.04
26	0.88	0.93	2.38	0.63	0.89	13.57	1.44	1.74	0.90	1.06	1.04	0.86	2.21	0.46	0.73	0.92	0.53	0.89
	CF (30−60 cm)																	
1	0.84	1.20	0.93	1.03	1.00	0.56	1.24	1.70	0.33	0.92	1.52	1.49	2.34	2.08	1.74	1.02	1.40	0.83
2	0.86	1.21	0.86	1.08	1.03	0.58	1.07	1.68	0.50	0.90	1.37	1.48	2.10	1.82	1.59	1.07	1.42	1.01
3	0.88	1.24	0.98	1.13	1.03	0.58	1.38	1.75	0.32	0.94	1.93	1.59	2.48	1.84	1.72	1.06	1.45	0.93
4	0.94	1.21	0.81	1.06	1.09	0.58	1.28	1.97	0.31	0.99	1.47	1.31	2.75	1.35	1.97	0.85	1.45	0.93
5	1.04	1.26	0.86	1.26	1.21	0.59	1.25	1.72	0.80	1.04	1.53	1.68	2.06	1.63	1.90	1.07	1.59	0.99
6	0.98	1.17	0.78	1.12	1.14	0.54	1.22	1.32	0.29	0.98	1.19	1.50	1.46	1.30	1.59	1.04	1.49	0.92
7	1.12	1.32	0.79	1.22	1.40	0.60	1.22	1.75	0.33	1.09	1.14	1.65	2.33	1.32	1.76	1.02	1.67	0.96
8	1.05	1.18	0.84	1.19	1.30	0.59	1.10	2.38	0.32	1.04	1.07	1.66	4.02	1.10	2.27	1.02	1.54	0.94
9	1.05	1.21	0.84	1.09	1.23	0.64	1.41	3.30	0.35	1.18	0.95	1.74	5.87	0.91	2.60	0.94	1.61	1.11
10	0.93	1.28	0.84	1.05	1.06	0.58	1.12	1.92	0.35	0.97	1.12	2.00	2.50	3.15	1.94	1.41	1.42	1.47
11	0.97	1.19	0.84	1.08	1.12	0.57	1.11	1.77	0.75	0.99	1.09	1.73	2.34	1.26	2.23	1.12	1.48	0.99
12	0.93	1.26	1.04	1.19	1.12	0.61	1.47	1.81	0.36	1.00	1.99	1.68	2.63	1.64	1.85	1.01	1.50	0.92
13	0.83	1.18	1.17	1.06	1.02	0.53	1.21	1.46	0.32	0.91	1.74	1.46	1.92	1.74	1.50	1.00	1.43	0.87
14	1.00	1.27	0.90	1.16	1.14	0.58	1.36	1.81	0.36	1.07	1.82	1.68	2.22	1.64	1.82	1.03	1.55	0.97
15	0.94	0.73	1.21	0.92	0.79	0.46	0.97	2.34	0.31	0.88	0.97	1.93	2.96	0.66	2.16	1.50	1.42	0.72
16	1.17	1.12	1.19	1.09	0.96	0.51	1.18	2.30	0.35	0.97	1.25	1.82	2.66	1.63	2.19	0.83	1.61	0.90
17	1.13	0.77	1.28	1.14	0.94	0.52	1.24	2.35	0.36	0.97	1.34	1.95	2.92	1.41	2.09	0.84	1.60	0.90
18	1.02	1.05	1.06	0.95	0.92	0.53	1.04	2.63	0.35	0.97	0.95	2.19	3.09	1.17	2.19	0.77	1.53	0.91
19	1.05	1.47	1.23	1.54	1.15	0.60	1.19	3.15	0.33	1.12	1.75	1.75	2.68	1.62	2.80	1.02	1.55	0.97
20	1.06	1.31	2.20	0.99	1.17	0.57	1.20	2.68	0.39	1.06	0.87	1.71	2.93	1.27	2.38	0.90	1.50	0.98
21	0.12	0.10	0.25	0.47	0.08	0.20	0.82	0.44	0.24	0.23	1.03	0.87	0.64	0.79	0.64	3.11	0.01	0.63
22	0.83	1.20	0.93	0.89	0.87	0.54	1.03	2.65	0.33	0.95	1.26	1.85	3.28	1.07	2.43	3.13	1.28	0.76
23	1.14	1.43	1.16	0.96	0.78	1.08	1.22	1.96	0.41	1.08	1.19	2.14	2.32	0.65	2.59	0.94	1.12	0.95
24	1.00	1.21	1.41	0.75	0.74	1.09	1.32	2.20	0.37	1.07	0.88	1.50	3.16	0.40	2.35	0.71	0.98	0.96
25	1.00	1.22	0.97	0.86	0.69	1.04	1.21	2.01	0.45	1.03	1.19	1.94	2.67	0.68	2.28	0.97	0.97	0.91
26	0.88	1.09	0.96	0.73	0.52	1.01	1.18	2.58	0.36	1.01	1.29	1.86	3.19	0.44	2.29	1.75	0.86	0.82

Table 8.3.6 BAC of the elements in different grapevine parts from the soil (0–30 cm and 30–60 cm) (Experiment 2; Milićević et al., 2018a)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
BAC seed/soil (0-30)																						
M	1.1E-05	1.3E-04	0.14	0.085	/	4.76	2.4E-04	1.5E-04	1.1E-04	0.14	3.6E-04	2.03	/	0.73	0.0059	0.06	5.9E-04	3.7E-05	4.2E-04	0.065	8.0E-06	0.080
Min	1.3E-06	2.5E-05	0.08	0.029	/	0.53	4.6E-05	3.6E-06	5.6E-05	0.09	7.7E-05	1.70	/	0.09	4.0E-04	0.02	3.5E-05	2.3E-05	1.8E-05	0.014	5.8E-07	0.004
Max	1.1E-04	4.6E-04	0.18	0.213	/	7.65	2.6E-03	6.9E-04	1.8E-03	0.31	4.8E-04	3.40	/	1.12	0.0186	0.58	5.7E-03	0.093	5.7E-03	0.174	3.2E-04	0.136
BAC seed/soil (30-60)																						
M	1.1E-05	1.3E-04	0.14	0.074	/	4.47	7.7E-04	1.5E-04	1.6E-04	0.16	3.3E-04	2.49	/	0.80	0.0062	0.05	4.8E-04	3.9E-05	3.1E-04	0.064	9.4E-06	0.085
Min	1.4E-06	2.0E-05	0.06	0.016	/	0.28	8.2E-05	3.9E-06	5.2E-05	0.07	8.0E-05	1.55	/	0.08	5.0E-04	0.01	3.7E-05	9.7E-06	1.0E-05	0.009	3.9E-07	0.004
Max	1.1E-04	1.0E-03	0.56	0.189	/	8.12	7.8E-03	7.5E-04	0.0016	0.36	1.6E-03	13.6	/	1.30	0.0180	0.69	4.9E-03	0.062	4.4E-03	0.169	5.6E-04	0.149
BAC pulp/soil (0-30)																						
M	1.3E-05	3.2E-05	0.07	0.005	/	0.24	3.7E-05	2.6E-06	4.09E-05	0.02	6.6E-05	1.00	/	0.08	3.0E-04	0.04	1.2E-04	3.3E-04	2.8E-04	0.007	2.7E-05	0.038
Min	3.6E-06	6.6E-06	0.03	0.002	/	0.06	1.1E-05	1.9E-06	2.7E-05	0.01	2.6E-05	0.65	/	0.05	1.0E-04	0.00	2.0E-05	1.0E-05	8.7E-06	0.002	3.8E-07	0.019
Max	9.6E-05	1.6E-04	0.11	0.012	/	0.50	1.1E-03	0.0021	0.022	0.59	3.0E-04	1.66	/	0.10	0.0021	0.08	8.4E-04	0.042	1.2E-03	0.019	7.1E-05	0.077
BAC pulp/soil (30-60)																						
M	1.6E-05	2.9E-05	0.06	0.005	/	0.24	1.2E-04	2.6E-06	3.8E-05	0.02	6.1E-05	1.20	/	0.08	2.0E-04	0.04	9.4E-05	2.7E-04	1.8E-04	0.006	1.9E-05	0.038
Min	3.8E-06	6.1E-06	0.03	0.001	/	0.02	3.5E-05	1.9E-06	2.2E-05	0.01	2.3E-05	0.67	/	0.05	1.0E-04	0.00	1.8E-05	7.0E-06	6.0E-06	0.001	2.59E-07	0.018
Max	1.1E-04	8.6E-04	0.43	0.011	/	0.48	7.3E-03	3.2E-03	0.019	0.66	2.9E-04	6.52	/	0.10	0.0020	0.10	7.4E-04	0.074	7.7E-04	0.022	4.3E-03	0.106
BAC skin/soil (0-30)																						
M	7.6E-06	1.6E-05	0.16	0.014	/	0.41	9.2E-05	4.1E-05	4.1E-05	0.03	1.2E-04	2.23	/	0.12	8.0E-04	0.02	2.8E-04	1.6E-05	2.8E-04	0.018	1.7E-05	0.024
Min	3.4E-06	1.4E-06	0.01	0.008	/	0.06	1.0E-05	1.0E-06	2.4E-05	0.02	9.3E-05	1.26	/	0.09	3.0E-04	0.00	1.9E-05	9.2E-06	4.4E-06	0.009	3.6E-07	0.014
Max	1.5E-04	2.4E-04	0.23	0.033	/	0.67	0.075	0.018	6.8E-04	0.12	2.2E-04	2.93	/	0.16	0.0028	0.03	1.2E-03	0.051	0.0070	0.046	1.3E-04	0.045
BAC skin/soil (30-60)																						
M	8.6E-06	1.5E-05	0.17	0.013	/	0.42	2.3E-04	4.3E-05	4.2E-05	0.03	1.2E-04	2.49	/	0.11	0.0008	0.01	2.6E-04	1.3E-05	1.9E-04	0.017	1.1E-05	0.024
Min	3.6E-06	1.3E-06	0.01	0.005	/	0.03	3.4E-05	1.2E-06	2.1E-05	0.02	8.9E-05	1.35	/	0.08	3.0E-04	0.00	1.5E-05	6.2E-06	2.8E-06	0.003	2.3E-07	0.013
Max	1.6E-04	2.0E-04	0.74	0.028	/	0.74	0.24	0.016	6.2E-04	0.13	5.8E-04	13.2	/	0.18	0.0021	0.03	1.0E-03	0.030	0.004	0.039	1.4E-03	0.056
BAC leaf/soil (0-30)																						
M	0.0007	0.006	0.46	0.068	1.3E-03	3.48	0.0005	0.0028	0.0015	0.10	0.0026	0.57	0.006	0.32	0.05	0.07	0.0095	0.0110	3.4E-03	0.971	0.0015	0.189
Min	0.0003	0.002	0.31	0.034	1.1E-04	0.45	0.0001	0.0012	0.0004	0.06	0.0013	0.37	0.002	0.16	0.02	0.01	0.0002	0.0008	9.5E-05	0.380	0.0006	0.116
Max	0.0014	0.024	1.12	0.131	9.3E-03	5.88	0.0028	0.0090	0.0230	0.14	0.0056	0.86	0.009	0.54	0.17	0.15	0.0562	0.1355	0.15	1.499	0.0035	0.332
BAC leaf/soil (30-60)																						
M	0.0009	0.005	0.48	0.059	1.4E-03	3.96	0.0016	0.0030	0.0015	0.11	0.003	0.65	0.006	0.32	0.05	0.07	0.0080	0.0083	2.7E-03	0.884	0.0011	0.198
Min	0.0003	0.002	0.26	0.022	9.5E-05	0.29	0.0003	0.0016	0.0002	0.06	0.001	0.34	0.002	0.16	0.02	0.01	0.0001	0.0004	6.0E-05	0.151	0.0004	0.107
Max	0.0061	0.086	1.68	0.117	9.8E-03	6.63	0.0108	0.0095	0.0201	0.16	0.022	3.40	0.023	0.50	0.22	0.15	0.0471	0.3514	0.10	1.326	0.0833	0.330

Table 8.3.7 Calculated RF between the parts of the grapevine exposed to air (the grapevine leaves and grape skin) *versus* these parts which are not directly exposed to air pollution (the grape pulp and seed) (Experiment 2; Milićević et al., 2018a)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
RF leaf/seed																						
Med.	67	33.50	3.17	0.72	/	0.77	2.79	40.41	5.92	0.69	6.34	0.29	/	0.41	7.53	0.94	18.6	71.8	4.47	10.7	151.27	2.29
Min	4.85	11.7	2.27	0.49	/	0.49	0.07	8.57	0.21	0.23	3.53	0.12	/	0.27	4.95	0.10	0.38	0.12	0.13	5.36	1.98	1.21
Max	418	712	11.29	1.31	/	1.22	53.3	1324	259	0.99	39.2	0.39	/	3.41	104	3.23	243	755	498	46.7	3925	43.2
RF leaf/pulp																						
Med.	51.61	212	7.82	11.84	/	15.6	8.73	993	35.81	5.59	32.61	0.61	/	3.84	208	1.65	64.3	130	17.44	133	112.51	4.58
Min	5.12	30.2	3.89	7.55	/	9.02	0.50	0.59	0.02	0.21	12.1	0.24	/	2.21	61.33	0.51	0.86	0.08	0.48	28.6	11.93	3.07
Max	290	1011	22.25	20.8	/	25.9	193	4207	461	13.8	115	1.09	/	6.11	448	95.21	1387	2428	17023	280	4705	11.1
RF skin/seed																						
Med.	0.76	0.16	1.16	0.17	/	0.09	0.25	0.45	0.41	0.19	0.36	1.06	/	0.14	0.11	0.21	0.57	0.44	0.61	0.23	0.98	0.26
Min	0.05	0.02	0.00	0.11	/	0.06	0.01	0.01	0.02	0.08	0.26	0.38	/	0.11	0.07	0.00	0.03	0.00	0.02	0.10	0.01	0.15
Max	112	8.27	1.54	0.32	/	0.15	400	103	6.40	0.87	1.57	1.25	/	1.12	1.85	0.98	17.4	1570	195	1.07	55.7	3.92
RF skin/pulp																						
Med.	0.77	0.83	2.57	2.72	/	1.75	1.21	5.21	1.07	1.83	2.07	2.23	/	1.55	3.18	0.35	4.42	0.85	1.18	2.73	0.72	0.71
Min	0.07	0.08	0.00	1.41	/	0.87	0.08	0.01	0.001	0.04	0.35	0.78	/	1.06	0.45	0.01	0.02	0.00	0.12	0.50	0.22	0.31
Max	28.03	17.47	3.81	5.15	/	3.52	2160	6521	15.4	5.75	4.11	3.17	/	2.00	5.26	3.42	45.0	3006	90.6	7.32	325	1.05

Table 8.3.8 Non-carcinogenic and carcinogenic risk assessment for workers in the vineyard chronically exposed to the potentially toxic elements in the soil (Experiment 2; Milićević et al., 2018a)

	Non-carcinogenic risk – HI (Hazardous Index)				Carcinogenic risk – R			
Sample	HQ(o)	HQ(i)	HQ(d)	HI	R(o)	R(i)	R(d)	R
1	0.28	0.007	0.005	0.29	3.36E-05	8.40E-07	1.02E-06	3.54E-05
2	0.26	0.007	0.005	0.27	2.94E-05	7.19E-07	9.68E-07	3.11E-05
3	0.27	0.008	0.005	0.28	3.02E-05	7.53E-07	9.47E-07	3.19E-05
4	0.27	0.007	0.005	0.28	3.12E-05	7.79E-07	9.57E-07	3.29E-05
5	0.26	0.006	0.005	0.28	2.82E-05	6.87E-07	9.41E-07	2.98E-05
6	0.25	0.006	0.005	0.26	2.46E-05	5.70E-07	9.28E-07	2.60E-05
7	0.27	0.006	0.005	0.29	2.90E-05	7.03E-07	9.81E-07	3.07E-05
8	0.28	0.007	0.005	0.29	3.63E-05	9.48E-07	9.39E-07	3.82E-05
9	0.32	0.007	0.005	0.33	4.47E-05	1.22E-06	9.58E-07	4.68E-05
10	0.27	0.006	0.006	0.28	3.62E-05	8.71E-07	1.23E-06	3.83E-05
11	0.27	0.007	0.005	0.28	3.22E-05	8.03E-07	9.96E-07	3.40E-05
12	0.28	0.008	0.005	0.30	3.03E-05	7.51E-07	9.78E-07	3.20E-05
13	0.27	0.007	0.004	0.28	2.85E-05	7.10E-07	8.87E-07	3.00E-05
14	0.28	0.007	0.005	0.29	3.16E-05	7.99E-07	9.37E-07	3.34E-05
15	0.29	0.006	0.004	0.30	4.62E-05	1.32E-06	7.23E-07	4.82E-05
16	0.28	0.006	0.004	0.29	3.44E-05	9.12E-07	8.38E-07	3.61E-05
17	0.28	0.008	0.003	0.29	3.13E-05	8.72E-07	6.03E-07	3.27E-05
18	0.27	0.006	0.004	0.28	3.75E-05	1.01E-06	8.40E-07	3.93E-05
19	0.27	0.006	0.005	0.28	3.37E-05	8.21E-07	1.11E-06	3.56E-05
20	0.28	0.006	0.005	0.29	3.60E-05	9.13E-07	1.04E-06	3.79E-05
21	0.29	0.006	0.005	0.30	4.03E-05	1.05E-06	1.05E-06	4.24E-05
22	0.26	0.006	0.005	0.28	3.78E-05	9.79E-07	1.00E-06	3.98E-05
23	0.27	0.006	0.005	0.28	3.26E-05	7.92E-07	1.09E-06	3.45E-05
24	0.28	0.006	0.005	0.29	3.51E-05	8.83E-07	1.05E-06	3.70E-05
25	0.29	0.006	0.005	0.30	3.52E-05	8.88E-07	1.04E-06	3.71E-05
26	0.27	0.006	0.005	0.28	3.56E-05	9.10E-07	1.00E-06	3.76E-05

Table 8.3.9 Non-carcinogenic assessment for consumers of grapevine (adults and children) and consumers of wine (adults) from the investigated vineyard and carcinogenic risk (R) assessment applying adjustable formula for children and adults (Experiment 2; Milićević et al., 2018a)

Consumers			
Sample	HI male	HI children	R adjustable
1	0.23	0.10	1.03E-05
2	0.24	0.08	7.13E-06
3	0.43	0.10	9.27E-06
4	0.32	0.10	8.24E-06
5	0.22	0.08	7.99E-06
6	0.18	0.07	8.42E-06
7	0.18	0.06	6.69E-06
8	0.13	0.05	6.53E-06
9	0.20	0.08	6.93E-06
10	0.15	0.06	7.39E-06
11	0.24	0.10	8.55E-06
12	0.21	0.07	7.53E-06
13	0.17	0.06	5.90E-06
14	0.42	0.12	9.11E-06
15	0.20	0.06	1.37E-05
16	0.24	0.09	9.92E-06
17	0.64	0.11	6.44E-06
18	0.34	0.08	8.07E-06
19	0.34	0.09	6.44E-06
20	0.19	0.07	6.71E-06
21	0.16	0.06	8.05E-06
22	0.19	0.06	7.99E-06
white wine	0.22	/	7.05E-07
red wine	0.21	/	2.881E-06

8.4 Appendix 4: Experiment 3

Table 8.4.1 Descriptive statistics of physicochemical parameters: pH−acidity (-), SOM−soil organic matter (%), CEC−cation exchange capacity (cmol kg^{-1}), N (%), C (%) and H (%) (Experiment 3; Milićević et al., 2018b)

0–30 cm and 30–60 cm		April	May	June	July	August
pH (H_2O)	M	7.51	7.86	7.51	7.57	7.29
	SD	0.38	0.32	0.33	0.74	0.76
	Range	7.06–7.88	7.70–8.43	7.28–7.74	6.54–8.57	7.06–7.88
	C			6.57		
	SD			0.16		
pH (1 M KCl)	M	6.46	6.85	6.29	6.08	6.42
	SD	0.24	0.38	0.33	0.81	0.87
	Range	6.33–6.92	6.56–7.47	6.06–6.52	5.15–7.31	6.33–6.92
	C			5.09		
	SD			0.15		
pH (0.1 M $CaCl_2$)	M	6.73	7.27	6.74	6.68	6.91
	SD	0.21	0.33	0.43	0.77	0.83
	Range	6.53–7.06	6.98–7.77	6.43–7.04	5.60–7.71	6.53–7.06
	C			5.57		
	SD			0.12		
SOM (%)	M	0.81	0.96	0.89	0.96	0.79
	SD	0.08	0.13	0.27	0.12	0.17
	Range	0.76–0.81	0.72–1.03	0.70–1.09	0.81–2.06	0.48–0.96
	C			0.92		
	SD			0.09		
CEC (cmol kg^{-1})	M	28.45	27.89	28.02	27.64	26.58
	SD	3.10	2.02	3.76	2.29	2.88
	Range	22.03–30.34	24.03–28.35	22.13–32.20	23.92–29.34	22.72–31.34
	C			22.06		
	SD			2.63		
N (%)	M	0.13	0.16	0.16	0.14	0.14
	SD	0.02	0.03	0.02	0.01	0.03
	Range	0.11–0.16	0.10–0.16	0.14–0.21	0.13–0.15	0.08–0.16
	C			0.16		
	SD			0.04		
C (%)	M	1.68	1.57	1.71	1.37	1.61
	SD	0.22	0.50	0.27	0.09	1.04
	Range	1.36–1.87	1.04–2.25	0.52–1.98	1.29–1.49	1.06–4.09
	C			1.65		
	SD			0.41		
H (%)	M	0.80	0.77	0.80	0.81	0.77
	SD	0.04	0.07	0.05	0.03	0.11
	Range	0.79–0.89	0.74–0.89	0.62–0.98	0.78–0.85	0.53–0.84
	C			0.74		
	SD			0.05		

Table 8.4.2 Descriptive statistics of pseudo-total element concentrations (mg kg^{-1}) in soil (n=182) through the grapevine season (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April (0-30 cm)																							
M	66429	13.2	40.5	227	1.87	7933	2.14	24.7	138.7	45.1	41517	10691	8746	1181	685	111.5	317	16.8	58.7	2.8	38.5	61.4	84.1
Min	56451	10.6	30.8	187	1.67	5013	2.00	19.7	89.3	36.1	37535	9273	7158	885	624	61.2	243	13.2	17.5	2.4	31.3	54.4	68.7
Max	75969	15.2	59.9	251	2.11	47888	3.10	33.0	264.8	117.8	58350	11991	11670	1625	875	188.4	480	27.1	92.0	4.5	87.6	71.0	179.1
April (30-60 cm)																							
M	65071	17.2	24.1	294	1.73	7293	0.28	23.5	164.9	47.2	43082	9198	9207	1041	595	141.5	328	36.0	122.1	5.7	93.5	115.2	82.3
Min	52445	11.9	13.7	202	1.33	5193	0.20	18.9	95.0	37.2	39115	8078	7277	750	496	82.8	190	23.9	60.4	4.1	60.8	96.3	73.2
Max	75762	19.1	61.3	335	1.99	83337	0.37	28.9	223.8	111.6	48020	10284	12042	1470	670	223.7	539	49.7	539.2	6.7	133.3	124.1	85.7
May (0-30 cm)																							
M	67933	13.8	41.7	237	1.91	7654	2.21	26.2	132.9	44.4	42023	10351	8724	1090	675	110.0	380	20.1	96.8	3.1	40.7	63.9	85.8
Min	54581	9.9	30.1	189	1.60	4764	1.94	19.4	118.5	36.7	38752	8563	7176	899	536	61.1	258	13.2	73.0	2.2	22.7	53.7	76.2
Max	137629	28.3	77.0	515	4.15	43391	4.43	50.6	284.1	123.8	85368	20743	16245	2619	1522	212.7	813	36.3	266.3	6.2	85.5	131.9	182.4
May (30-60 cm)																							
M	66044	16.5	21.0	306	1.80	6835	0.27	24.0	160.0	48.8	43194	9254	8816	1106	691	132.4	361	35.8	108.9	5.1	62.5	109.8	79.9
Min	44414	11.6	15.8	160	1.13	4420	0.18	15.9	98.8	39.5	34007	6654	6942	808	430	69.0	244	19.6	75.4	4.5	86.8	83.8	65.8
Max	75431	20.5	77.0	348	2.19	118262	0.45	28.9	523.0	87.1	47903	10929	11154	1597	866	277.2	494	45.0	751.0	8.3	43.6	126.0	90.7
June (0-30 cm)																							
M	66812	14.3	37.8	250	1.95	7492	2.18	25.2	140.5	41.7	42516	10393	8432	1170	687	106.1	332	18.6	104.4	3.0	43.7	62.8	79.9
Min	57661	13.4	34.2	196	1.73	5437	2.14	22.4	123.3	39.2	40651	9723	7702	871	592	63.1	306	13.1	60.4	2.7	36.2	57.1	74.0
Max	73511	16.6	50.3	265	2.10	51011	2.35	29.3	180.8	72.6	45122	11797	9644	1477	773	188.1	486	29.8	126.7	3.8	86.6	67.6	86.0
June (30-60 cm)																							
M	61786	16.8	17.8	291	1.80	6931	0.34	22.3	144.6	43.6	42292	8434	7872	1163	724	128.7	361	35.7	124.2	5.0	87.2	111.1	79.7
Min	30793	10.0	14.5	124	0.87	5003	0.24	15.6	94.4	28.2	29682	5542	6962	776	592	88.3	235	10.8	80.2	3.8	70.1	49.4	45.5
Max	70495	20.5	31.6	328	1.98	189642	0.39	23.9	172.6	99.6	46426	10863	10380	1503	802	169.2	515	53.5	1060	6.7	130.3	119.7	104.8
July (0-30 cm)																							
M	67305	13.4	37.2	241	1.91	7098	2.18	25.3	124.4	43.9	42813	12104	8925	1104	675	106.5	362	17.7	102.4	3.1	40.8	63.2	81.0
Min	55298	9.8	29.8	188	1.62	5093	1.92	20.2	96.6	37.1	39704	10255	7174	875	492	61.6	232	10.7	59.2	2.4	27.8	53.6	68.7
Max	78817	16.5	64.5	370	2.10	65679	2.42	31.4	200.5	138.6	48140	9263	12553	3261	844	197.8	487	25.7	124.2	3.9	94.5	69.7	92.4
July (30-60 cm)																							
M	70186	15.6	38.0	303	2.63	7127	1.19	22.9	149.3	40.7	44353	9629	9022	991	802	129.6	324	27.1	53.8	1.2	52.8	61.9	87.6
Min	44538	10.4	17.9	188	1.84	5278	0.26	16.5	39.9	32.1	37807	7508	7501	701	573	69.4	22	18.1	10.7	0.3	31.7	38.5	63.4
Max	81124	19.0	52.9	345	3.10	113533	2.07	177.1	219.4	112.0	46864	11142	13023	1488	1005	373.6	464	59.9	141.1	38.2	173.0	180.6	98.2
August (0-30 cm)																							
M	71509	13.7	41.6	262	2.00	8298	3.91	25.9	137.8	43.2	42299	11402	9006	1084	756	106.2	336	16.7	91.2	3.2	42.6	66.8	82.2
Min	60784	8.6	33.7	215	1.70	5342	3.56	21.3	93.9	38.1	40138	10304	7731	904	701	62.0	241	13.0	52.5	2.6	28.5	57.4	71.5
Max	81568	17.6	59.8	284	2.41	48874	4.40	33.6	221.0	82.9	47782	13109	12152	1681	866	199.3	553	27.7	145.7	4.2	93.2	71.7	101.1
August (30-60 cm)																							
M	68017	15.5	39.8	298	2.18	7281	1.25	25.6	145.3	38.2	43092	9421	8833	1106	766	130.3	333	23.8	71.4	4.8	48.2	96.6	82.9
Min	8536	1.2	11.0	129	0.16	4764	0.44	17.4	34.4	26.9	10236	1634	6390	767	395	32.6	47	11.5	21.9	1.6	36.4	0.9	55.8
Max	81384	19.0	96.3	424	2.84	96473	1.39	31.2	256.8	90.2	52079	12646	12629	1755	1000	298.1	536	54.4	142.1	6.9	147.7	107.7	131.2
Local back ground (C)																							
Mean	69453	14.47	27.4	315	1.97	5796	0.24	19	70	46.6	42692	10040	8538	1013	685	56.9	347.3	30.6	87.3	4.6	46.5	105	83.1
SD	3806	1.43	9.0	30	0.12	211	0.03	4.0	19	6.4	878	1336	307	95	92	2.3	1.3	2.6	1.1	1	3.1	13	2
RSD %	5.5	9.9	32.0	9.4	5.9	3.6	9.4	20.5	27.0	14.0	2.1	13.3	3.6	9.4	13.5	3.9	0.4	8.4	1.2	21.7	6.5	12.1	2.4
MAC		25	50				3		100	100						50		100					

Table 8.4.3 Descriptive statistics of element concentrations (mg kg^{-1}) (Median–M, Minimum–Min and Maximum–Max) extracted from the topsoil and the subsoil samples by deionised H_2O during 2 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April 0-30 cm																							
M	9.0	<DL	0.51	0.66	0.0037	137	0.0007	0.0068	0.02	0.30	2.67	5.99	15.0	0.35	11.7	0.042	1.04	0.034	10.0	<DL	0.249	0.009	0.68
Min	2.5	/	0.08	0.26	0.0008	97	0.0004	0.0001	0.005	0.03	0.57	3.12	3.5	0.12	7.9	0.012	0.57	0.010	2.7	/	0.119	0.007	0.07
Max	24.9	/	4.75	2.14	0.0101	412	0.0015	0.0242	0.07	1.48	7.64	11.44	64.6	1.75	46.3	0.194	2.21	0.086	20.2	/	4.689	0.025	2.49
April 30-60 cm																							
M	10.7	<DL	0.59	0.93	0.0037	162	0.0008	0.0050	0.01	0.64	1.53	3.91	12.1	0.45	17.1	0.038	0.70	0.055	10.7	<DL	0.286	0.010	0.44
Min	3.5	/	0.11	0.28	0.0018	68	0.0004	0.0006	0.004	0.22	0.52	2.18	3.7	0.10	8.6	0.005	0.37	0.014	4.0	/	0.137	0.007	0.12
Max	41.0	/	14.17	2.45	0.0117	380	0.0014	0.0337	0.03	8.30	10.76	7.45	39.2	1.23	54.3	0.224	1.65	0.355	18.0	/	2.653	0.075	1.86
Maj 0-30 cm																							
M	8.6	<DL	0.11	0.51	0.0034	127	0.0009	0.0095	0.01	0.70	2.03	4.94	11.3	0.34	6.0	0.085	1.24	0.028	25.2	<DL	0.113	0.017	1.20
Min	0.4	/	0.10	0.05	0.0032	42	0.0008	0.0088	0.003	0.08	0.25	2.11	4.1	0.04	3.0	0.035	0.04	0.017	3.4	/	0.055	0.016	0.08
Max	37.6	/	14.47	1.58	0.0065	226	0.0017	0.0337	0.30	1.38	13.94	14.54	25.3	1.80	17.9	0.230	5.54	0.086	38.0	/	0.456	0.035	4.81
May 30-60 cm																							
M	8.9	<DL	0.19	0.68	0.0035	45	0.0009	0.0095	0.01	0.78	1.86	2.06	11.6	0.39	6.3	0.085	0.63	0.035	27.9	<DL	0.096	0.018	1.16
Min	1.2	/	0.10	0.04	0.0032	200	0.0008	0.0086	0.00	0.12	0.54	0.87	3.4	0.04	3.7	0.015	0.04	0.017	4.8	/	0.058	0.016	0.07
Max	71.9	/	29.02	1.46	0.0035	225	0.0009	0.0236	0.41	1.13	32.85	6.58	19.3	1.33	35.9	0.197	2.89	0.092	40.3	/	0.318	0.036	5.30
June 0-30 cm.																							
M	27.8	<DL	0.01	0.49	0.0024	82	0.0100	0.0092	0.05	0.67	11.27	4.88	11.4	0.36	5.7	0.110	0.91	0.029	10.2	<DL	0.083	0.036	0.45
Min	14.3	/	0.00	0.09	0.0024	52	0.0044	0.0007	0.02	0.33	3.53	3.00	4.3	0.19	3.6	0.047	0.63	0.007	3.3	/	0.053	0.016	0.003
Max	52.7	/	0.24	1.09	0.0024	178	0.0235	0.0149	0.12	0.93	25.05	18.37	19.4	1.18	13.1	0.210	1.80	0.051	18.9	/	0.175	0.063	1.02
June 30-60 cm																							
M	32.8	<DL	0.00	0.62	0.0024	83	0.0092	0.0076	0.07	0.75	12.55	5.51	11.1	0.55	7.6	0.148	0.62	0.039	12.3	<DL	0.078	0.035	0.94
Min	13.0	/	0.00	0.15	0.0023	40	0.0036	0.0016	0.02	0.30	3.77	0.03	4.7	0.22	4.6	0.050	0.40	0.017	5.6	/	0.038	0.016	0.16
Max	93.5	/	0.18	1.35	0.0024	589	0.0195	0.0175	0.18	4.79	42.32	12.88	22.8	1.20	12.2	0.451	1.61	0.105	21.8	/	1.007	0.098	4.64
July 0-30 cm																							
M	10.0	<DL	0.41	0.54	0.0023	78	0.0096	0.0064	0.02	0.53	3.49	6.32	10.3	0.42	4.8	0.100	1.03	0.041	9.7	<DL	0.074	0.022	0.13
Min	4.8	/	0.10	0.11	0.0003	35	0.0022	0.0005	0.01	0.36	1.52	2.25	4.0	0.06	2.0	0.032	0.45	0.010	5.4	/	0.031	0.006	0.003
Max	44.9	/	1.92	1.07	0.0024	150	0.0165	0.0142	0.12	1.10	20.26	9.82	15.5	1.05	18.6	0.231	2.15	0.307	17.2	/	0.114	0.059	2.23
July 30-60 cm																							
M	18.1	<DL	0.41	1.40	0.0024	58	0.0059	0.0059	0.04	0.78	6.98	3.61	8.1	0.19	7.3	0.084	0.38	0.023	14.2	<DL	0.063	0.026	0.24
Min	6.0	/	0.14	0.27	0.0023	15	0.0011	0.0011	0.01	0.34	2.31	0.69	3.4	0.12	2.4	0.012	0.05	0.001	8.7	/	0.016	0.004	0.003
Max	46.7	/	0.98	3.65	0.0024	196	0.0126	0.0126	0.11	1.34	20.52	5.95	14.5	0.82	47.6	0.840	1.08	0.175	27.1	/	0.113	0.056	3.89
August 0-30 cm																							
M	11.1	<DL	0.01	0.62	0.0038	139	0.0011	0.0065	0.02	0.63	3.17	5.44	11.9	0.30	6.9	0.053	1.10	0.042	9.3	<DL	0.251	0.016	0.37
Min	1.2	/	0.00	0.29	0.0017	44	0.0007	0.0011	0.003	0.11	0.53	1.38	5.6	0.12	4.1	0.014	0.32	0.004	4.1	/	0.118	0.007	0.00
Max	110.8	/	1.04	2.49	0.0110	256	0.0098	0.0217	0.33	1.23	72.76	15.04	31.9	0.71	21.9	0.429	2.98	1.355	15.0	/	0.517	0.134	2.12
August 30-60 cm																							
M	19.4	<DL	0.01	0.96	0.0053	132	0.0015	0.0098	0.03	0.62	4.92	3.68	13.4	0.32	8.5	0.068	0.62	0.075	10.0	<DL	0.266	0.018	0.86
Min	5.2	/	0.00	0.26	0.0017	49	0.0007	0.0023	0.02	0.32	1.33	1.30	4.1	0.18	4.4	0.027	0.19	0.004	5.8	/	0.087	0.006	0.23
Max	65.3	/	20.73	3.24	0.0152	248	0.0080	0.0239	0.22	3.83	39.01	9.25	24.9	1.19	69.3	1.293	1.91	0.544	17.7	/	0.391	0.079	6.84

Table 8.4.4 Descriptive statistics of element concentrations (mg kg^{-1}) (Median–M, Minimum–Min and Maximum–Max) extracted from the topsoil and the subsoil samples by deionised H_2O during 16 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April0-30 cm																							
M	8.5	<DL	0.43	0.79	0.0041	193	0.002	0.005	0.009	0.44	2.11	7.1	18.7	0.67	31.7	0.06	0.82	0.024	11.3	<DL	0.310	0.014	0.26
Min	1.8	/	0.18	0.16	0.00027	112	0.001	0.003	0.004	0.19	0.53	4.3	5.5	0.09	19.6	0.01	0.37	0.002	6.7	/	0.212	0.001	0.07
Max	60.4	/	6.48	3.09	0.01218	288	0.005	0.015	0.184	2.42	48.89	15.5	35.1	3.46	90.2	0.24	2.57	0.093	17.8	/	0.484	0.114	0.92
April 30-60 cm																							
M	12.6	<DL	0.53	1.04	0.00531	189	0.002	0.003	0.012	0.48	2.35	4.8	15.1	0.80	32.4	0.07	0.59	0.020	12.0	<DL	0.287	0.017	0.30
Min	3.0	/	0.18	0.25	0.00073	81	0.001	0.003	0.002	0.22	0.73	2.9	5.7	0.13	25.3	0.01	0.16	0.010	3.8	/	0.192	0.001	0.00
Max	60.7	/	12.28	3.53	0.01601	241	0.004	0.016	0.144	5.03	38.71	14.6	31.7	2.23	164.3	0.22	1.27	0.108	23.1	/	0.438	0.079	0.78
Maj 0-30 cm																							
M	8.7	<DL	0.39	0.50	0.00339	150	0.001	0.011	0.015	0.35	1.40	5.6	14.8	0.34	5.6	0.07	0.87	0.048	3.5	<DL	0.190	0.017	0.63
Min	1.0	/	0.10	0.04	0.00328	23	0.001	0.006	0.003	0.01	0.09	0.8	2.3	0.01	2.2	0.02	0.06	0.018	0.1	/	0.002	0.015	0.10
Max	34.3	/	17.10	3.23	0.00724	252	0.002	0.270	0.358	1.23	13.68	21.1	38.8	2.25	14.3	0.28	3.68	0.096	25.1	/	0.429	0.036	1.61
May 30-60 cm																							
M	10.1	<DL	0.42	0.71	0.0034	144	0.001	0.011	0.020	0.29	2.72	2.3	15.5	0.38	6.2	0.07	0.30	0.028	2.9	<DL	0.155	0.017	0.58
Min	1.1	/	0.10	0.02	0.00325	20	0.001	0.009	0.003	0.00	0.17	0.5	2.5	0.01	1.9	0.00	0.02	0.015	0.2	/	0.008	0.016	0.07
Max	65.9	/	7.65	4.35	0.00844	219	0.003	0.064	0.474	1.22	9.37	13.9	37.9	3.23	35.9	0.27	3.09	0.148	24.7	/	0.438	0.047	1.83
June 0-30 cm																							
M	13.1	<DL	0.08	0.76	0.00237	56	0.050	0.400	0.024	0.75	5.25	4.6	14.7	0.53	3.4	0.22	0.42	0.033	14.1	<DL	0.112	0.029	0.89
Min	8.0	/	0.02	0.05	0.00158	3.8	0.004	0.332	0.005	0.61	1.27	3.0	6.1	0.06	1.9	0.02	0.14	0.014	9.8	/	0.083	0.015	0.51
Max	34.7	/	0.64	1.36	0.0024	107	0.051	0.711	0.033	1.37	6.75	10.3	20.3	1.01	8.7	0.57	0.94	0.110	21.1	/	0.156	0.049	1.56
June 30-60 cm																							
M	14.7	<DL	0.14	0.62	0.00236	36	0.050	0.518	0.021	0.99	4.53	3.3	11.2	0.43	3.9	0.19	0.28	0.054	13.6	<DL	0.102	0.030	0.89
Min	5.0	/	0.01	0.08	0.00169	2.6	0.004	0.255	0.005	0.51	0.98	2.2	5.3	0.11	2.1	0.01	0.10	0.020	7.9	/	0.058	0.009	0.00
Max	55.0	/	0.34	1.55	0.00241	311	0.051	4.235	0.064	8.42	15.56	5.5	22.0	1.27	7.5	0.86	0.67	0.148	18.1	/	0.502	0.051	3.07
July 0-30 cm																							
M	21.5	<DL	0.40	0.81	0.00699	85	0.011	0.462	0.033	0.91	7.35	6.4	16.8	0.59	3.1	0.21	0.85	0.097	14.6	<DL	0,185	0.023	0.54
Min	5.6	/	0.19	0.11	0.0023	10	0.003	0.330	0.017	0.65	3.65	2.3	6.9	0.04	0.6	0.01	0.36	0.042	9.8	/	0,084	0.006	0.08
Max	54.7	/	0.65	1.85	0.01339	235	0.019	1.918	0.063	2.76	15.03	10.1	24.5	1.63	18.4	0.80	2.11	0.234	24.4	/	0,481	0.049	1.99
July 30-60 cm																							
M	22.8	<DL	0.28	0.93	0.00918	88	0.008	0.425	0.036	0.84	8.03	4.3	18.0	0.40	3.6	0.13	0.44	0.096	12.0	<DL	0.181	0.030	0.64
Min	8.1	/	0.07	0.09	0.00384	28	0.003	0.232	0.018	0.46	4.02	2.0	6.7	0.07	0.6	0.02	0.14	0.020	7.5	/	0.090	0.012	0.03
Max	61.5	/	1.01	3.00	0.01445	269	0.030	9.276	0.070	18.54	15.59	8.5	34.0	2.24	60.6	0.73	2.06	1.631	19.5	/	0.391	0.060	2.52
August 0-30 cm																							
M	10.3	<DL	0.01	0.27	0.00027	42	0.001	0.027	0.038	0.44	3.78	3.4	19.3	0.26	2.8	0.10	0.40	0.065	9.0	<DL	0.138	0.004	0.16
Min	1.2	/	0.01	0.08	0.00026	7	0.001	0.003	0.013	0.06	1.33	0.5	6.5	0.03	1.9	0.01	0.02	0.012	3.4	/	0.051	0.004	0.00
Max	46.1	/	3.61	1.80	0.0078	196	0.003	0.074	0.272	1.13	43.48	9.5	43.7	0.71	35.6	5.14	1.46	0.189	13.0	/	0.381	0.043	1.27
August 30-60 cm																							
M	12.6	<DL	0.06	0.45	0.00027	36	0.001	0.026	0.054	0.48	8.18	2.0	12.4	0.22	3.1	0.09	0.18	0.067	7.6	<DL	0.108	0.004	0.13
Min	1.0	/	0.00	0.07	0.00026	6	0.000	0.003	0.004	0.14	0.78	0.2	5.6	0.06	2.0	0.01	0.01	0.001	1.6	/	0.043	0.004	0.00
Max	49.4	/	10.36	2.76	0.00261	61	0.005	0.070	0.224	3.05	38.02	12.9	44.4	1.30	41.2	1.03	0.89	0.183	16.2	/	0.263	0.044	1.83

Table 8.4.5 Descriptive statistics of element concentrations (mg kg^{-1}) (Median–M, Minimum–Min and Maximum–Max) extracted from the topsoil and the subsoil samples by 0.01 $CaCl_2$ during 3 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April0-30 cm																						
M	1.61	<DL	0.21	1.95	0.0008	0.0020	0.0050	0.0051	0.176	1.50	32.3	224	1.72	9.5	0.043	0.36	<DL	1.61	<DL	2.96	0.008	0.138
Min	1.07	/	0.01	0.84	0.0002	0.0011	0.0011	0.0036	0.034	1.11	17.8	56	0.19	6.2	0.003	0.14	/	1.07	/	2.14	0.004	0.002
Max	3.79	/	6.38	4.75	0.0024	0.0112	0.1026	0.0138	1.093	2.57	47.0	365	27.32	53.7	0.751	0.59	/	3.79	/	3.95	0.014	0.466
April 30-60 cm																						
M	1.46	<DL	0.82	2.22	0.0007	0.0022	0.0056	0.0071	0.105	1.67	17.5	256	2.24	14.1	0.072	0.24	<DL	1.46	<DL	3.23	0.006	0.070
Min	0.93	/	0.08	0.77	0.0002	0.0011	0.0009	0.0009	0.006	0.91	10.2	44	0.09	9.6	0.003	0.09	/	0.93	/	1.73	0.003	0.002
Max	4.01	/	18.05	4.30	0.0022	0.0127	0.0782	0.0677	0.501	14.90	45.1	356	29.62	95.6	0.835	0.66	/	4.01	/	3.96	0.015	0.759
Maj 0-30 cm																						
M	4.27	<DL	0.31	1.15	0.0010	0.0009	0.0050	0.0094	0.022	2.50	26.1	156	2.51	7.1	0.059	0.27	<DL	4.55	<DL	1.99	0.005	0.192
Min	0.62	/	0.02	0.55	0.0000	0.0005	0.0008	0.0014	0.006	0.30	11.3	47	0.03	2.1	0.000	0.10	/	1.75	/	0.82	0.000	0.001
Max	5.99	/	16.06	3.53	0.0030	0.0075	0.1442	0.4113	0.261	3.61	65.3	405	26.17	27.9	11.691	1.95	/	12.32	/	3.75	0.023	16.883
May 30-60 cm																						
M	3.32	<DL	0.43	1.14	0.0010	0.0009	0.0054	0.0085	0.008	1.91	11.5	164	3.29	10.1	0.114	0.12	<DL	4.42	<DL	1.85	0.005	0.012
Min	1.83	/	0.01	0.48	0.0001	0.0006	0.0001	0.0023	0.006	0.86	3.5	38	0.00	2.8	0.004	0.01	/	1.26	/	0.81	0.000	0.001
Max	6.89	/	30.95	2.91	0.0028	0.0133	0.1100	0.4076	0.686	5.47	28.4	254	21.75	88.9	2.383	0.67	/	7.86	/	2.57	0.012	4.157
June 0-30 cm.																						
M	8.29	<DL	0.63	1.94	0.0008	0.0011	0.0064	0.0210	0.042	4.11	27.3	222	2.49	14.9	0.104	0.44	<DL	4.07	<DL	0.00	0.010	0.119
Min	4.28	/	0.01	0.84	0.0001	0.0009	0.0005	0.0048	0.006	2.17	11.9	71	0.10	8.9	0.011	0.14	/	1.62	/	0.00	0.002	0.002
Max	10.86	/	2.37	4.30	0.0040	0.0125	0.1112	0.0542	13.682	5.23	52.6	373	26.41	22.7	0.864	0.98	/	8.91	/	0.00	0.022	0.960
June 30-60 cm																						
M	8.32	<DL	0.82	1.62	0.0008	0.0010	0.0063	0.0174	0.006	4.10	14.6	223	1.37	18.6	0.058	0.39	<DL	2.64	<DL	0.00	0.009	0.099
Min	2.30	/	0.08	0.65	0.0003	0.0009	0.0017	0.0042	0.006	1.44	7.9	42	0.18	6.9	0.017	0.12	/	0.18	/	0.00	0.002	0.002
Max	11.27	/	1.19	5.11	0.0034	0.0180	0.1120	0.0312	3.404	5.92	30.3	385	45.62	35.4	1.148	0.42	/	4.82	/	0.16	0.016	0.279
July 0-30 cm																						
M	8.11	<DL	0.01	2.12	0.0008	0.0010	0.0062	0.0147	0.183	3.16	30.6	235	3.75	18.3	0.186	0.56	<DL	3.61	<DL	0.18	0.008	0.674
Min	5.88	/	0.01	0.81	0.0000	0.0003	0.0023	0.0079	0.006	2.33	14.7	55	0.32	-0.1	0.008	0.95	/	2.38	/	0.00	0.002	0.002
Max	11.98	/	11.22	4.90	0.0042	0.0285	0.0991	0.0311	770.117	5.14	45.8	352	34.26	64.8	0.895	2.87	/	7.08	/	0.99	0.015	1.996
July 30-60 cm																						
M	9.23	<DL	0.01	2.61	0.0008	0.0009	0.0058	0.0188	0.154	3.50	19.5	269	1.92	26.9	0.124	0.37	<DL	3.71	<DL	0.04	0.008	0.548
Min	5.39	/	0.01	0.67	0.0001	0.0002	0.0003	0.0034	0.006	2.74	10.2	55	0.24	3.3	0.005	0.18	/	1.68	/	0.00	0.000	0.120
Max	12.52	/	0.62	5.05	0.0047	0.0141	0.1162	0.0484	6.760	48.14	33.1	368	24.08	142.9	1.170	0.87	/	7.86	/	1.51	0.016	1.472
August 0-30 cm																						
M	1.73	<DL	0.01	1.80	0.0010	0.0031	0.0022	0.0059	0.130	1.58	29.4	0	194.32	0.6	9.322	0.04	0.271494	1.73	<DL	2.93	0.006	0.002
Min	0.80	/	0.01	0.77	0.0002	0.0011	0.0009	0.0007	0.005	0.74	9.1	0	59.36	0.0	3.922	0.00	0.051933	0.80	/	1.25	0.003	0.002
Max	3.19	/	4.68	4.26	0.0025	0.0123	0.0335	0.0110	3.042	2.46	46.9	0	336.86	12.8	36.391	0.96	0.79131	3.19	/	3.89	0.013	0.150
August 30-60 cm																						
M	1.88	<DL	0.01	1.72	0.0007	0.0028	0.0030	0.0053	0.051	1.55	17.5	0	234.36	0.3	13.405	0.03	0.138636	1.88	<DL	2.98	0.006	0.002
Min	0.98	/	0.01	0.77	0.0002	0.0011	0.0009	0.0007	0.001	0.86	6.8	0	44.22	0.0	5.633	0.00	0.06977	0.98	/	1.43	0.003	0.002
Max	4.72	/	24.68	5.49	0.0078	0.0205	0.1136	0.0856	0.295	4.08	46.6	0	356.84	26.1	41.01	1.61	0.438309	4.72	/	4.11	0.011	0.643

Table 8.4.6 Descriptive statistics of element concentrations (mg kg^{-1}) (Median–M, Minimum–Min and Maximum–Max) extracted from the topsoil and the subsoil samples by 0.1 mol L^{-1} NH_4NO_3 during 2 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April0-30 cm																							
M	2.08	<DL	0.0031	36.0	0.0008	3234	<DL	0.0023	0.006	0.027	1.85	134	310	3.15	9.2	0.063	0.096	<DL	0.921	<DL	6.79	0.006	0.026
Min	0.79	/	0.0030	23.9	0.0002	2229	/	0.0004	0.003	0.007	0.86	86	78	0.52	6.3	0.010	0.021	/	0.452	/	5.28	0.001	0.001
Max	6.47	/	1.1099	57.0	0.0157	3765	/	0.1342	0.017	0.274	4.94	174	498	41.37	47.8	1.293	0.147	/	2.401	/	8.80	0.017	0.538
April 30-60 cm																							
M	3.17	<DL	0.0222	36.9	0.0012	3207	<DL	0.0041	0.008	0.025	1.92	99	346	4.02	11.9	0.076	0.052	<DL	0.947	<DL	6.72	0.008	0.024
Min	0.47	/	0.0031	24.3	0.0002	2109	/	0.0009	0.002	0.002	0.79	71	63	0.19	8.3	0.007	0.021	/	0.368	/	4.96	0.001	0.001
Max	7.53	/	5.9736	58.8	0.0114	3920	/	0.1023	0.024	0.126	6.05	158	535	47.44	79.6	1.471	0.271	/	2.217	/	8.18	0.018	0.376
Maj 0-30 cm																							
M	4.26	<DL	0.8745	25.9	0.0020	1739	<DL	0.0098	0.016	0.037	1.88	18	77	2.96	9.0	0.117	0.047	0.0212	1.141	<DL	3.17	0.089	0.243
Min	2.74	0	0.0336	8.4	0.0001	1160	/	0.0021	0.008	0.003	0.53	4	16	0.02	5.0	0.018	0.044	0.0004	0.003	/	1.47	0.024	0.002
Max	8.03	0	11.0044	41.7	0.0021	2320	/	0.1971	0.218	46.951	5.94	36	141	25.20	30.6	2.346	0.225	0.0549	3.977	/	5.18	0.200	1.949
May 30-60 cm																							
M	4.16	<DL	0.7074	25.7	0.0020	1729	<DL	0.0097	0.019	0.038	2.04	32	68	2.28	7.7	0.164	0.046	0.0216	1.497	<DL	3.16	0.088	0.260
Min	2.75	0	0.0017	8.1	0.0019	1112	/	0.0003	0.009	0.007	0.75	12	19	0.09	4.6	0.017	0.004	0.0024	0.003	/	1.47	0.000	0.002
Max	9.59	0	4.7722	54.1	0.0039	2980	/	0.2765	0.214	0.829	6.75	64	155	30.60	21.0	1.741	0.949	0.0428	6.378	/	5.52	0.177	2.311
June 0-30 cm.																							
M	2.27	0.016566	0.0067	24.2	0.0198	28459	<DL	0.0067	0.007	0.005	0.83	82	146	1.82	15.2	0.110	0.043	0.0141	0.081	<DL	7.44	0.123	0.215
Min	1.89	0.016377	0.0066	12.2	0.0091	14955	/	0.0049	0.003	0.004	0.39	49	20	0.05	8.5	0.008	0.043	0.0115	0.080	/	4.81	0.063	0.001
Max	4.94	0.016734	0.0068	32.8	0.0239	35567	/	0.1022	0.017	1.098	3.62	133	222	20.59	23.0	0.929	0.044	0.0142	0.082	/	10.72	0.647	0.865
June 30-60 cm																							
M	1.84	0.016442	0.0067	23.2	0.0244	28512	<DL	0.0062	0.005	0.004	0.53	56	122	0.83	16.2	0.052	0.043	0.0140	0.080	<DL	6.30	0.097	0.048
Min	1.51	0.015961	0.0065	6.3	0.0148	18480	/	0.0048	0.003	0.001	0.19	18	8	0.08	9.2	0.005	0.042	0.0136	0.078	/	1.51	0.061	0.001
Max	3.04	0.01666	0.0068	30.1	0.0298	40857	/	0.1323	0.010	0.250	0.97	85	205	42.93	25.5	1.560	0.043	0.0142	0.081	/	9.45	1.179	0.959
July 0-30 cm																							
M	2.04	0.016388	0.0067	18.4	0.0221	27148	<DL	0.0053	0.005	0.026	0.59	92	101	2.22	14.1	0.124	0.043	0.0139	0.080	<DL	7.45	0.136	0.134
Min	1.57	0.016054	0.0065	13.1	0.0117	19271	/	0.0048	0.003	0.004	0.18	52	21	0.14	10.0	0.006	0.042	0.0136	0.078	/	3.85	0.062	0.001
Max	3.85	0.016606	0.0067	32.9	0.0287	37025	/	0.1534	0.015	0.476	1.37	129	232	39.27	20.9	1.294	0.043	0.0141	0.081	/	10.07	1.114	0.796
July 30-60 cm																							
Median	2.36	0.016462	0.0067	24.1	0.0191	27148	<DL	0.0050	0.006	0.004	0.83	71	141	1.17	18.2	0.117	0.043	0.0140	0.080	<DL	7.89	0.070	0.003
Min	1.42	0.015661	0.0064	9.1	0.0060	19271	/	0.0048	0.000	0.001	0.14	35	14	0.05	6.3	0.000	0.041	0.0133	0.076	/	2.30	0.062	0.001
Max	7.49	0.045142	0.0068	34.8	0.0317	37025	/	0.1799	0.020	0.143	2.76	92	271	26.77	25.5	2.060	0.043	0.1284	0.081	/	10.61	0.856	0.891
August 0-30 cm																							
M	1.96	<DL	0.0031	37.2	0.0012	2991	<DL	0.0018	0.005	0.041	1.56	126	281	1.08	9.1	0.051	0.065	<DL	1.693	<DL	5.96	0.006	0.052
Min	0.45	/	0.0030	20.0	0.0002	2029	/	0.0001	0.001	0.005	0.58	74	67	0.07	5.2	0.003	0.020	/	0.897	/	3.80	0.002	0.001
Max	6.06	/	0.4391	66.9	0.0078	3902	/	0.0408	0.013	4.151	3.66	181	558	21.21	30.9	1.713	0.293	/	5.440	/	7.82	0.010	0.434
August 30-60 cm																							
M	2.63	<DL	0.0031	40.7	0.0013	3064	<DL	0.0018	0.006	0.067	1.71	91	331	0.67	13.6	0.045	0.040	<DL	1.705	<DL	6.43	0.006	0.045
Min	0.35	/	0.0030	21.3	0.0002	1960	/	0.0001	0.001	0.002	0.72	68	57	0.05	5.4	0.004	0.020	/	0.477	/	4.37	0.003	0.001
Max	24.69	/	7.7141	56.5	0.0342	4513	/	0.1432	0.017	43.849	4.42	163	553	33.31	86.3	2.475	0.210	/	4.117	/	9.12	0.012	0.800

Table 8.4.7 Descriptive statistics of element concentrations (mg kg^{-1}) (Median–M, Minimum–Min and Maximum–Max) extracted from the topsoil and the subsoil samples by 0.05 mol L^{-1} Na_2EDTA during 1 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April 0-30 cm																								
M	318	0.141	0.300	14.9	0.0038	3121	0.075	5.56	0.029	7.1	167	44	0.082	199	308	/	7.6	7.2	8.5	0.5	<DL	5.1	1.1	3.44
Min	76	0.040	0.017	4.4	0.0001	1932	0.044	2.16	0.005	4.7	68	26	0.053	78	205	/	3.9	2.4	4.5	0.4	/	3.6	0.5	0.95
Max	437	0.312	9.560	20.0	0.0231	16035	0.106	6.83	0.268	36.7	289	74	0.100	272	423	/	16.3	29.4	11.1	13.2	/	18.0	2.6	6.28
April 30-60 cm																								
M	313	0.121	0.125	15.6	0.0067	2834	0.057	5.56	0.020	6.1	155	23	0.078	201	291	/	6.5	1.5	7.4	0.5	<DL	4.8	1.0	1.81
Min	26	0.028	0.017	3.6	0.0019	1797	0.016	0.27	0.005	1.7	26	14	0.065	63	61	/	1.0	0.1	2.6	0.4	/	2.8	0.1	0.34
Max	469	0.309	25.726	19.4	0.0241	15950	0.135	8.70	0.213	33.2	466	62	0.114	267	504	/	21.8	22.6	15.2	15.1	/	16.4	3.8	4.11
Maj 0-30 cm																								
M	560	0.137	0.316	21.8	0.0043	3329	0.075	7.35	0.302	9.3	7	56	0.107	229	408	/	9.2	25.7	11.8	30.1	<DL	5.4	2.5	6.42
Min	222	0.082	0.031	8.9	0.0000	1880	0.024	5.51	0.117	4.6	6	27	0.052	93	252	/	4.1	7.3	7.5	4.2	/	4.0	1.5	0.79
Max	1149	0.347	17.099	51.3	0.0362	24613	0.150	18.17	10.979	50.0	18	119	0.201	531	909	/	22.9	135.3	20.0	48.6	/	28.8	4.9	11.37
May 30-60 cm																								
M	561	0.105	0.347	21.9	0.0097	3073	0.055	7.29	0.275	7.2	373	31	0.111	237	381	/	8.2	13.6	9.6	28.4	<DL	5.8	2.1	2.07
Min	71	0.085	0.004	7.0	0.0022	1963	0.025	2.90	0.060	2.9	74	7	0.048	84	246	/	5.1	0.2	4.9	5.7	/	3.7	0.3	0.26
Max	745	0.247	32.655	29.9	0.0287	28469	0.122	13.62	4.701	32.8	802	78	0.169	321	683	/	17.0	55.5	14.0	46.0	/	38.1	4.7	8.19
June 0-30 cm.																								
M	233	0.077	0.017	9.5	0.0018	2507	0.033	3.45	0.005	4.1	129	21	0.045	196	210	/	4.0	4.4	4.7	0.4	<DL	5.7	0.7	1.92
Min	57	0.041	0.016	3.9	0.0003	1451	0.002	1.33	0.003	0.0	48	9	0.019	43	134	/	2.6	1.3	2.9	0.4	/	0.0	0.3	0.004
Max	291	0.220	4.722	15.4	0.0160	17010	0.079	6.34	0.063	15.6	247	64	0.061	264	341	/	7.8	20.3	8.3	16.7	/	17.0	2.0	5.03
June 30-60 cm																								
M	182	0.040	0.017	8.1	0.0021	2209	0.005	3.38	0.009	0.0	98	6	0.033	87	170	/	3.7	1.0	2.7	0.4	<DL	3.9	0.5	0.004
Min	8.6	0.013	0.016	2.3	0.0001	517	0.0001	0.13	0.005	0.0	30	0	0.002	70	33	/	0.3	0.1	0.1	0.4	/	0.0	0.1	0.004
Max	477	0.086	1.818	10.6	0.0188	14421	0.050	5.69	0.059	14.1	301	20	0.055	209	351	/	6.0	8.9	7.2	12.6	/	16.9	1.8	5.25
July 0-30 cm																								
M	240	0.052	0.016	9.4	0.0018	2216	0.036	4.00	0.005	4.4	143	26	0.054	159	218	/	4.8	7.8	4.2	0.4	<DL	5.5	0.8	3.27
Min	0.53	0.006	0.016	0.001	0.0014	1.88	0.002	0.002	0.003	0.0	0	3	0.0001	1	0	/	0.0	0.1	0.03	0.4	/	0.01	0.0	0.004
Max	541	1.332	1.501	16.9	0.0179	13884	0.077	6.86	0.078	27.1	329	49	0.100	258	408	/	13.9	38.4	9.7	14.2	/	13.4	2.3	6.64
July 30-60 cm																								
M	275	0.051	0.016	8.6	0.0045	2543	0.020	3.74	0.005	2.4	131	16	0.070	181	178	/	4.1	2.1	4.2	0.4	<DL	5.3	0.7	2.23
Min	23	0.013	0.016	3.2	0.0013	1091	0.002	0.32	0.004	0.0	32	1	0.020	76	65	/	1.1	0.1	1.3	0.4	/	2.9	0.1	0.004
Max	457	0.196	0.017	18.3	0.0285	17412	0.089	5.25	0.020	14.3	239	30	0.088	311	392	/	10.0	15.2	6.5	21.5	/	16.7	1.6	6.04
August 0-30 cm																								
M	322	0.182	0.017	14.7	0.0025	3976	0.077	6.03	0.005	6.5	179	37	0.079	209	351	/	8.3	9.8	7.4	0.5	<DL	4.9	1.2	2.34
Min	62	0.003	0.016	4.4	0.0018	1926	0.038	1.58	0.005	4.1	63	10	0.060	68	207	/	3.2	2.6	3.8	0.4	/	3.1	0.5	0.89
Max	461	0.366	17.382	20.2	0.0286	19065	0.228	7.94	0.038	23.9	283	68	0.096	300	486	/	13.6	72.4	10.7	17.9	/	19.2	2.6	5.95
August 30-60 cm																								
M	306	0.160	0.017	15.1	0.0043	3216	0.058	5.73	0.005	5.6	170	19	0.076	206	292	/	6.6	3.2	6.5	0.5	<DL	4.4	1.0	1.17
Min	28	0.006	0.015	4.3	0.0009	2140	0.007	0.22	0.004	1.4	26	3	0.051	60	47	/	1.4	0.1	2.1	0.4	/	1.6	0.1	0.005
Max	507	0.313	34.067	21.2	0.0338	19240	0.144	8.80	0.750	394.1	335	59	0.101	331	538	/	13.6	33.6	11.3	11.3	/	21.3	2.5	7.77

Table 8.4.8 Descriptive statistics of element concentrations (mg kg^{-1}) (Median−M, Minimum−Min and Maximum−Max) extracted from the topsoil and the subsoil samples by 0.11 mol L^{-1} CH_3COOH during 16 h extraction (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April0-30 cm																							
M	45.6	<DL	0.90	21.8	0.146	1310	0.013	0.300	0.094	0.010	13.1	90.6	339	49.6	11.3	6.9	4.8	0.035	0.27	<DL	5.8	0.014	0.744
Min	35.7	/	0.13	13.7	0.039	826	0.005	0.070	0.035	0.010	8.1	50.8	155	37.4	7.1	4.6	0.9	0.008	0.26	/	4.9	0.003	0.002
Max	64.1	/	12.19	25.9	0.199	3345	0.042	0.559	0.165	3.025	15.7	129.1	421	94.6	57.2	29.6	17.3	0.088	2.41	/	48.2	0.024	1.818
April 30-60 cm																							
M	42.1	<DL	1.26	22.7	0.160	1167	0.014	0.264	0.108	0.010	12.7	61.6	322	48.8	13.5	8.0	1.2	0.042	0.27	<DL	5.9	0.019	0.426
Min	17.3	/	0.15	12.2	0.003	702	0.002	0.027	0.053	0.010	9.7	46.0	128	18.5	7.1	4.8	0.2	0.035	0.27	/	3.9	0.001	0.002
Max	114.0	/	27.70	27.1	0.213	3579	0.050	0.592	0.274	3.495	16.9	105.1	424	120.5	109.0	55.3	3.7	0.158	0.56	/	81.0	0.043	1.349
Maj 0-30 cm																							
Mn	35.9	0.053	0.88	19.6	0.150	1094	0.015	0.506	0.076	0.011	9.3	90.2	316	62.3	6.2	2.8	7.5	0.043	11.32	<DL	5.5	0.020	0.928
Min	14.9	0.001	0.15	15.2	0.019	617	0.000	0.119	0.025	0.010	1.2	51.4	150	45.3	0.3	1.8	1.4	0.020	2.73	/	4.1	0.003	0.002
Max	82.6	0.164	22.18	40.5	0.337	6472	0.053	1.842	4.483	3.486	28.6	244.9	659	181.4	29.6	6.5	48.0	0.149	23.66	/	47.4	0.067	5.980
May 30-60 cm																							
M	26.7	0.038	1.02	20.0	0.160	1086	0.009	0.363	0.079	0.011	5.9	52.5	319	49.8	9.2	2.4	1.5	0.033	9.57	<DL	5.5	0.010	0.464
Min	6.3	0.008	0.10	12.6	0.014	662	0.001	0.022	0.009	0.010	0.4	23.4	141	31.4	4.0	1.5	0.1	0.002	0.74	/	3.8	0.000	0.002
Max	54.6	0.148	40.14	23.9	0.197	11451	0.079	0.838	2.106	3.355	17.9	149.3	468	352.3	109.0	4.5	11.3	0.162	22.14	/	87.4	0.068	4.918
June 0-30 cm.																							
M	41.6	0.045	0.03	18.1	0.013	28459	0.022	0.297	0.121	0.414	8.1	83.1	286	38.2	10.6	2.0	0.1	0.033	0.33	<DL	3.6	0.019	0.692
Min	33.7	0.011	0.03	12.0	0.002	14955	0.013	0.022	0.057	0.010	5.9	55.5	123	27.8	2.0	1.3	0.1	0.001	0.31	/	2.8	0.018	0.006
Max	50.4	0.047	0.03	20.3	0.022	35567	0.063	0.543	0.165	4.907	12.5	155.3	349	107.3	19.0	3.2	0.1	0.096	0.34	/	35.5	0.030	2.340
June 30-60 cm																							
M	39.9	0.045	0.03	18.3	0.013	28512	0.018	0.309	0.108	0.063	8.4	52.7	271	40.5	9.6	2.0	0.1	0.034	0.33	<DL	3.3	0.019	0.652
Min	12.1	0.011	0.03	5.0	0.001	18480	0.010	0.112	0.055	0.009	6.9	40.7	92	20.1	6.1	1.1	0.1	0.019	0.31	/	2.2	0.018	0.005
Max	58.6	0.046	0.48	21.3	0.037	40857	0.033	0.557	0.183	15.595	15.2	93.2	358	107.1	28.0	3.1	0.1	0.239	0.34	/	70.8	0.052	3.972
July 0-30 cm																							
M	48.4	0.051	0.03	17.9	0.013	27148	0.031	0.320	0.118	0.220	10.0	94.2	276	36.3	8.7	2.1	0.1	0.032	17.40	<DL	3.5	0.019	1.601
Min	24.8	0.005	0.03	8.9	0.000	19271	0.018	0.013	0.053	0.009	5.9	27.9	114	23.6	1.0	1.2	0.1	0.002	10.28	/	0.9	0.018	0.093
Max	59.3	0.102	0.03	22.2	0.046	37025	0.178	0.710	0.243	12.38	11.5	144.0	374	118.1	43.2	3.6	0.1	0.394	21.99	/	33.5	0.048	4.134
July 30-60 cm																							
M	43.8	0.044	0.03	18.8	0.015	27148	0.026	0.266	0.124	0.238	9.4	69.4	302	31.6	17.4	1.6	0.1	0.034	6.60	<DL	3.7	0.019	1.199
Min	13.8	0.0002	0.03	10.4	0.003	19271	0.006	0.026	0.059	0.010	4.4	53.5	96	14.0	4.1	1.1	0.1	0.001	1.96	/	2.4	0.018	0.006
Max	66.2	0.083	0.03	23.1	0.049	37025	0.063	0.621	0.209	4.620	12.6	84.8	413	124.6	154.8	2.8	0.1	0.261	13.34	/	59.0	0.045	4.007
August 0-30 cm																							
M	44.2	<DL	0.06	22.0	0.158	1394	0.011	0.283	0.077	0.010	11.5	93.3	323	37.2	15.9	9.1	4.6	0.036	14.76	<DL	5.6	0.024	0.845
Min	26.7	/	0.01	14.6	0.035	762	0.002	0.030	0.039	0.010	5.7	42.6	156	21.6	11.3	6.9	0.7	0.015	5.98	/	4.1	0.009	0.130
Max	53.5	/	9.17	26.3	0.208	6442	0.048	0.427	0.150	19.26	15.4	138.8	421	111.4	43.5	22.7	31.1	0.254	24.35	/	54.9	0.042	3.029
August 30-60 cm																							
M	38.3	<DL	0.10	21.7	0.169	1192	0.010	0.267	0.076	0.010	10.3	61.9	323	35.1	21.8	12.1	0.9	0.036	13.77	<DL	5.7	0.022	0.646
Min	15.2	/	0.05	12.3	0.002	717	0.001	0.019	0.035	0.003	4.6	32.5	121	17.1	14.1	7.7	0.0	0.034	0.27	/	3.8	0.002	0.002
Max	57.8	/	36.00	27.1	0.214	6659	0.045	0.497	0.878	6.885	16.3	113.5	463	175.3	125.6	63.4	10.9	0.108	21.07	/	76.1	0.046	3.820

Table 8.4.9 Descriptive statistics of CF (-) calculated for PTEs (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	P	Pb	S	Sb	Sr	V	Zn
April 0-30 cm																			
M	0.96	0.91	1.48	0.72	0.95	8.93	1.28	1.99	0.99	0.97	1.17	1.96	0.91	0.55	0.67	0.62	0.83	0.59	1.01
Min	0.81	0.73	1.13	0.59	0.85	8.35	1.02	1.28	0.79	0.88	0.87	1.08	0.70	0.43	0.20	0.52	0.67	0.52	0.83
Max	1.09	1.05	2.19	0.80	1.07	12.94	1.71	3.79	2.58	1.37	1.60	3.31	1.38	0.89	1.05	0.98	1.88	0.68	2.15
April 30-60 cm																			
M	0.94	1.19	0.88	0.93	0.88	1.17	1.22	2.36	1.04	1.01	1.03	2.49	0.94	1.18	1.40	1.25	2.01	1.10	0.99
Min	0.76	0.82	0.50	0.64	0.68	0.86	0.98	1.36	0.82	0.92	0.74	1.45	0.55	0.78	0.69	0.89	1.31	0.92	0.88
Max	1.09	1.32	2.24	1.06	1.01	1.53	1.50	3.21	2.45	1.12	1.45	3.93	1.55	1.62	6.18	1.47	2.87	1.18	1.03
May 0-30 cm																			
M	0.98	0.95	1.52	0.75	0.97	9.21	1.36	1.90	0.97	0.98	1.08	1.93	1.10	0.66	1.11	0.68	0.87	0.61	1.03
Min	0.79	0.68	1.10	0.60	0.81	8.09	1.01	1.70	0.80	0.91	0.89	1.07	0.74	0.43	0.84	0.48	0.49	0.51	0.92
Max	1.98	1.96	2.81	1.63	2.11	18.51	2.62	4.07	2.71	2.00	2.58	3.73	2.34	1.19	3.05	1.35	1.84	1.26	2.19
May 30-60 cm																			
M	0.95	1.14	0.77	0.97	0.92	1.12	1.25	2.29	1.07	1.01	1.09	2.33	1.04	1.17	1.25	1.11	1.87	1.05	0.96
Min	0.64	0.80	0.58	0.51	0.57	0.76	0.83	1.42	0.87	0.80	0.80	1.21	0.70	0.64	0.86	0.99	0.94	0.80	0.79
Max	1.09	1.42	2.82	1.10	1.11	1.89	1.50	7.49	1.91	1.12	1.58	4.87	1.42	1.47	8.60	1.80	3.09	1.20	1.09
June 0-30 cm																			
M	0.96	0.99	1.38	0.79	0.99	9.08	1.31	2.01	0.91	1.00	1.15	1.86	0.96	0.61	1.20	0.65	0.94	0.60	0.96
Min	0.83	0.93	1.25	0.62	0.88	8.92	1.16	1.77	0.86	0.95	0.86	1.11	0.88	0.43	0.69	0.58	0.78	0.55	0.89
Max	1.06	1.15	1.84	0.84	1.07	9.82	1.52	2.59	1.59	1.06	1.46	3.30	1.40	0.98	1.45	0.83	1.86	0.65	1.03
June 30-60 cm																			
M	0.89	1.16	0.65	0.92	0.92	1.41	1.16	2.07	0.96	0.99	1.15	2.26	1.04	1.17	1.42	1.10	1.88	1.06	0.96
Min	0.44	0.69	0.53	0.39	0.44	1.02	0.81	1.35	0.62	0.70	0.77	1.55	0.68	0.35	0.92	0.82	1.51	0.47	0.55
Max	1.02	1.42	1.15	1.04	1.01	1.61	1.24	2.47	2.18	1.09	1.48	2.97	1.48	1.75	12.14	1.47	2.80	1.14	1.26
July 0-30 cm																			
M	0.97	0.93	1.36	0.77	0.97	9.12	1.31	1.78	0.96	1.00	1.09	1.87	1.04	0.58	1.17	0.69	0.88	0.60	0.97
Min	0.80	0.68	1.09	0.60	0.82	8.03	1.05	1.38	0.81	0.93	0.86	1.08	0.67	0.35	0.68	0.53	0.60	0.51	0.83
Max	1.13	1.14	2.36	1.18	1.07	10.09	1.63	2.87	3.04	1.13	3.22	3.47	1.40	0.84	1.42	0.85	2.03	0.67	1.11
July 30-60 cm																			
M	1.01	1.08	1.39	0.96	1.34	4.96	1.19	2.14	0.89	1.04	0.98	2.28	0.93	0.89	0.62	0.26	1.14	0.59	1.05
Min	0.64	0.72	0.65	0.60	0.94	1.10	0.86	0.57	0.70	0.89	0.69	1.22	0.06	0.59	0.12	0.06	0.68	0.37	0.76
Max	1.17	1.31	1.93	1.10	1.57	8.64	9.19	3.14	2.46	1.10	1.47	6.56	1.34	1.96	1.62	8.32	3.72	1.72	1.18
August 0-30 cm																			
M	1.03	0.95	1.52	0.83	1.02	16.34	1.34	1.97	0.95	0.99	1.07	1.87	0.97	0.54	1.05	0.69	0.92	0.64	0.99
Min	0.88	0.60	1.23	0.68	0.86	14.85	1.10	1.35	0.84	0.94	0.89	1.09	0.69	0.42	0.60	0.57	0.61	0.55	0.86
Max	1.17	1.22	2.19	0.90	1.22	18.35	1.74	3.17	1.82	1.12	1.66	3.50	1.59	0.91	1.67	0.92	2.00	0.68	1.22
August 30-60 cm																			
M	0.98	1.07	1.46	0.95	1.11	5.21	1.33	2.08	0.84	1.01	1.09	2.29	0.96	0.78	0.82	1.04	1.04	0.92	1.00
Min	0.12	0.09	0.40	0.41	0.08	1.82	0.90	0.49	0.59	0.24	0.76	0.57	0.14	0.37	0.25	0.34	0.78	0.01	0.67
Max	1.17	1.31	3.52	1.34	1.45	5.78	1.62	3.68	1.98	1.22	1.73	5.23	1.54	1.78	1.63	1.50	3.18	1.03	1.58

Table 8.4.10 MF% (Median–M) (-) for each of the elements (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
											0-30 cm 2 h H_2O												
M	0.016	/	0.38	0.23	0.16	1.16	0.043	0.03	0.017	1.239	0.008	14.7	0.13	0.030	0.93	0.068	0.31	0.18	11.2	/	0.30	0.029	0.72
											30-60 cm 2 h H_2O												
M	0.022	/	0.65	0.30	0.19	1.14	0.333	0.03	0.020	1.537	0.011	0.04	0.11	0.030	1.11	0.066	0.19	0.11	15	/	0.175	0.017	0.73
											0-30 cm 16 h H_2O												
M	0.017	0.16	0.63	0.26	0.177	0.92	0.06	0.10	0.020	1.38	0.010	14.4	0.18	0.030	0.61	0.094	0.19	0.30	13	/	0.41	0.028	0.56
											30-60 cm 16 h H_2O												
M	0.022	0.13	0.83	0.26	0.186	0.72	0.415	0.11	0.021	1.335	0.013	0.04	0.16	0.031	0.81	0.070	0.11	0.19	12.1	/	0.23	0.017	0.47
											0-30 cm $CaCl_2$												
M	0.01	/	0.16	0.68	0.04	/	0.06	0.02	0.01	0.23	0.01	77	2.2	0.10	1.6	0.06	0.11	/	3.44	/	4.40	0.01	0.13
											30-60 cm $CaCl_2$												
M	0.0060	/	0.54	0.58	0.043	/	0.34	0.02	0.007	0.14	0.0061	0.19	2.30	0.10	2.47	0.049	0.067	/	2.93	/	2.11	0.0067	0.10
											0-30 cm NH_4NO_3												
M	0.0036	/	0.02	11.8	0.11	39.8	/	0.021	0.005	0.078	0.0029	240	1.43	0.16	1.48	0.077	0.014	0.088	0.97	/	14.01	0.10	0.10
											30-60 cm NH_4NO_3												
M	0.0047	/	0.03	9.9	0.12	40.7	/	0.030	0.006	0.058	0.0032	0.75	1.40	0.12	2.04	0.053	0.013	0.052	0.68	/	8.25	0.06	0.11
											0-30 cm Na_2EDTA												
M	0.47	0.86	0.05	5.8	0.18	42.2	2.37	21.9	0.00	14.6	0.32	94	2.11	26.7	/	6.67	3.08	40.0	0.58	/	13.3	1.96	3.75
											30-60 cm Na_2EDTA												
M	0.46	0.58	0.08	4.4	0.33	41.0	7.19	21.38	0.01	12.1	0.38	0.21	2.08	25.4	/	4.74	1.02	19.8	0.76	/	8.12	1.32	2.18
											0-30 cm CH_3COOH												
M	0.06	0.33	0.25	8.0	6.77	18.6	0.82	1.24	0.066	0.026	0.024	239	3.30	3.83	1.59	2.93	0.727	0.22	11.7	1.36	12.9	0.032	1.25
											30-60 cm CH_3COOH												
M	0.058	0.28	0.69	6.7	6.02	17.4	2.94	1.19	0.061	0.026	0.022	0.63	3.54	3.51	2.38	2.26	0.156	0.14	8.0	0.80	8.10	0.020	0.83

Table 8.4.11 Descriptive statistics of Eri (i=As, Cd, Cr, Cu, Ni, Pb, and Zn) (-) and RI (-)for the topsoil and the subsoil (Experiment 3; Milićević et al., 2018b)

Eri	As	Cd	Cr	Cu	Ni	Pb	Zn	RI=ΣEri
April 0-30 cm								
M	4.56	268	3.97	4.95	9.79	2.74	1.01	295
Min	3.65	250	2.56	3.96	5.38	2.16	0.83	269
Max	5.25	388	7.59	12.92	16.55	4.44	2.15	437
April 30-60 cm								
M	5.93	35	4.73	5.18	12.43	5.88	0.99	70
Min	4.10	26	2.72	4.08	7.27	3.91	0.88	49
Max	6.61	46	6.41	12.23	19.65	8.12	1.03	100
May 0-30 cm								
M	4.76	276	3.81	4.87	9.66	3.28	1.03	304
Min	3.42	243	3.40	4.02	5.36	2.15	0.92	262
Max	9.79	555	8.14	13.57	18.67	5.93	2.19	613
May 30-60 cm								
M	5.70	34	4.58	5.35	11.63	5.86	0.96	68
Min	4.01	23	2.83	4.34	6.06	3.21	0.79	44
Max	7.09	57	14.98	9.55	24.34	7.36	1.09	121
June 0-30 cm								
M	4.96	272	4.03	4.57	9.31	3.04	0.96	299
Min	4.63	268	3.53	4.30	5.54	2.15	0.89	289
Max	5.74	295	5.18	7.95	16.52	4.88	1.03	336
June 30-60 cm								
M	5.82	42	4.14	4.78	11.30	5.83	0.96	75
Min	3.47	31	2.70	3.09	7.75	1.77	0.55	50
Max	7.08	48	4.95	10.92	14.86	8.75	1.26	96
July 0-30 cm								
M	4.65	273	3.56	4.82	9.35	2.90	0.97	300
Min	3.38	241	2.77	4.07	5.41	1.75	0.83	259
Max	5.72	303	5.74	15.20	17.36	4.20	1.11	352
July 30-60 cm								
M	5.38	149	4.28	4.46	11.38	4.43	1.05	180
Min	3.58	33	1.14	3.51	6.10	2.95	0.76	51
Max	6.55	259	6.29	12.28	32.80	9.79	1.18	328
August 0-30 cm								
M	4.74	490	3.95	4.73	9.33	2.72	0.99	517
Min	2.98	445	2.69	4.18	5.45	2.12	0.86	464
Max	6.09	551	6.33	9.09	17.50	4.53	1.22	595
August 30-60 cm								
M	5.37	156	4.16	4.19	11.44	3.90	1.00	186
Min	0.43	55	0.99	2.95	2.86	1.87	0.67	64
Max	6.57	173	7.36	9.89	26.17	8.89	1.58	234

Table 8.4.12 Descriptive statistics of BGI (-) representing the element absorptions in the topsoil (Experiment 3; Milićević et al., 2018b)

BGI	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Sr	V	Zn
April																							
M	1.01	0.81	1.74	0.79	1.09	0.94	7.81	1.04	0.88	0.93	0.97	0.00	0.95	1.02	1.19	0.83	1.05	0.49	0.41	0.51	0.46	0.56	1.03
Min	0.84	0.72	0.98	0.70	0.97	0.16	5.57	0.90	0.67	0.79	0.81	0.00	0.85	0.74	0.99	0.64	0.68	0.38	0.08	0.40	0.34	0.49	0.88
Max	1.15	0.89	2.25	1.01	1.25	1.35	11.06	1.57	1.47	1.37	1.35	0.00	1.06	1.59	1.41	0.93	1.58	0.67	1.31	0.80	0.66	0.62	2.17
May																							
M	1.03	0.86	1.77	0.82	1.09	1.09	8.05	1.08	0.82	0.96	0.98	0.00	1.00	1.02	0.98	0.86	1.11	0.58	0.90	0.59	0.48	0.58	1.10
Min	0.85	0.76	1.00	0.62	0.87	0.16	4.90	0.87	0.38	0.69	0.87	0.00	0.90	0.76	0.79	0.46	0.54	0.40	0.21	0.46	0.26	0.47	0.93
Max	2.35	1.82	4.44	1.77	2.46	2.73	16.96	2.27	2.25	2.57	2.27	0.01	2.30	2.24	2.31	2.03	2.19	1.03	2.00	1.36	1.05	1.28	2.58
June																							
M	1.06	0.86	2.01	0.84	1.11	1.02	6.47	1.14	0.92	1.00	0.99	0.00	1.02	1.08	0.96	0.82	1.00	0.56	0.82	0.55	0.52	0.58	1.01
Min	0.97	0.79	1.36	0.80	0.98	0.27	5.54	1.02	0.82	0.40	0.91	0.00	0.89	0.88	0.84	0.63	0.78	0.45	0.09	0.50	0.39	0.54	0.82
Max	1.87	1.41	3.24	1.58	1.98	2.01	8.98	1.77	1.92	1.96	1.52	0.01	1.25	1.48	1.11	1.14	1.33	1.22	1.41	1.01	0.72	1.16	1.78
July																							
M	0.98	0.86	1.04	0.80	0.70	1.01	1.83	1.07	0.85	1.07	0.97	0.00	0.98	1.10	0.85	0.84	1.10	0.59	1.80	2.82	0.83	1.02	0.96
Min	0.88	0.79	0.89	0.72	0.55	0.13	0.99	0.13	0.66	0.49	0.87	0.00	0.87	0.90	0.66	0.36	0.80	0.24	0.77	0.09	0.27	0.30	0.84
Max	1.24	1.00	1.98	1.23	1.08	2.18	7.71	1.38	3.55	1.39	1.12	0.01	1.12	3.34	1.17	1.11	11.28	0.86	9.56	10.11	1.11	1.73	1.09
August																							
M	1.03	0.88	1.02	0.86	0.91	1.06	3.16	1.05	0.85	1.11	0.97	1.17	0.99	0.97	0.99	0.80	1.08	0.73	1.31	0.64	0.89	0.68	0.98
Min	0.94	0.82	0.62	0.57	0.83	0.09	2.87	0.82	0.56	0.50	0.81	1.00	0.91	0.66	0.82	0.67	0.71	0.42	0.68	0.55	0.47	0.62	0.69
Max	1.22	1.10	1.13	0.94	1.09	1.38	3.83	1.30	1.21	1.50	1.12	1.43	1.16	1.34	1.29	1.13	1.50	1.26	3.31	0.77	1.05	0.75	1.36

Table 8.4.13 Descriptive statistics of BRAI (-) calculated for topsoil and subsoil using element concentrations extracted by Na_2EDTA (regular equation) and CH_3COOH (modify equation); The $BRAI_{probable}$ (using concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn) and $BRAI_{apparent}$ (using concentrations of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn) for both regular and modify equations are presented (Experiment 3; Milićević et al., 2018b)

	$BRAIEDTA_{probbable}$	$BRAIEDTA_{apparent}$	$BRAICH3COOH_{probbable}$	$BRAICH3COOH_{apparent}$
		April 0-30 cm		
M	1.49	1.55	1.00	1.00
Min	1.33	1.18	1.00	1.00
Max	1.76	1.68	1.40	1.13
		April 30-60 cm		
M	1.80	1.92	1.00	1.00
Min	1.16	1.27	1.00	1.00
Max	2.66	2.79	2.06	1.72
		May 0-30 cm		
M	1.59	1.79	1.00	1.00
Min	1.40	1.53	1.00	1.00
Max	1.87	1.97	1.00	1.00
		May30-60 cm		
M	2.04	2.22	1.00	1.00
Min	1.48	1.63	1.00	1.00
Max	2.66	3.08	1.46	1.40
		June 0-30 cm		
M	1.24	1.30	1.00	1.00
Min	1.09	1.06	1.00	1.00
Max	1.65	1.91	1.00	1.00
		June 30-60		
M	1.09	1.25	1.00	1.00
Min	1.00	1.00	1.00	1.00
Max	1.55	1.81	1.46	1.44
		July 0-30 cm		
M	1.25	1.28	1.00	1.00
Min	1.00	1.00	1.00	1.00
Max	1.50	1.67	1.00	1.00
		July 30-60 cm		
M	1.09	1.28	1.00	1.00
Min	1.00	1.00	1.00	1.00
Max	1.17	1.52	1.00	1.00
		August 0-30 cm		
M	1.41	1.59	1.09	1.05
Min	1.17	1.09	1.00	1.00
Max	1.87	1.82	2.00	1.36
		August 30-60		
M	1.24	1.51	1.04	1.00
Min	1.09	1.03	1.00	1.00
Max	1.87	1.82	2.00	1.36

Table 8.4.14 Descriptive statistic (Median−M, Minimum−Min and Maximum−Max) of element concentrations (mg kg^{-1}) in the leaf samples (n=75) collected through the entire grapevine season (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
										May											
M	138	0.043	30.5	7.6	0.00371	11371	0.0074	0.037	0.140	9.53	134	6595	1302	49	42	3.10	0.28	0.00	11	0.153	21.1
Min	98	0.016	14.2	3.2	0.00155	6625	0.0007	0.024	0.025	6.32	85	4757	1007	22	8	0.03	0.01	0.00	3	0.066	13.3
Max	186	0.105	74.6	17.2	0.01150	25175	0.0780	0.110	0.770	15.83	253	9590	1831	274	103	9.69	1.90	0.66	38	0.239	44.8
										June											
M	62	0.042	41.8	12.3	0.00245	20719	0.0020	0.031	0.078	8.67	115	7612	1983	41	121	1.40	0.14	0.01	26	0.055	23.1
Min	44	0.016	22.9	5.2	0.000004	14465	0.0004	0.019	0.045	5.41	103	6843	1701	25	10	0.03	0.01	0.00	13	0.001	16.3
Max	83	0.088	57.4	27.1	0.01620	27603	0.1653	0.039	0.175	14.47	137	10071	2651	234	191	2.09	3.91	0.01	40	0.095	30.1
										July											
M	91	0.094	30.6	13.8	0.00263	24198	0.0026	0.070	0.351	5.22	131	7762	2242	59	101	2.26	0.44	0.02	30	0.108	13.3
Min	67	0.035	16.6	5.4	0.00046	17848	0.0001	0.034	0.205	4.23	88	5716	1495	26	25	0.03	0.11	0.00	13	0.052	9.1
Max	139	0.205	47.9	28.3	0.01673	35906	0.0139	0.214	1.793	13.44	367	12095	3883	274	136	6.59	1.22	0.24	45	0.439	20.6
										August											
M	53	0.075	20.3	17.3	0.00236	29917	0.0019	0.074	0.203	4.40	102	7215	2816	55	54	1.76	0.15	0.01	45	0.052	15.7
Min	22	0.031	14.2	8.3	0.00025	25411	0.0004	0.033	0.049	3.21	56	4587	1954	27	5	0.03	0.01	0.00	18	0.000	11.2
Max	89	0.310	47.5	37.2	0.01919	39573	0.0108	0.249	2.835	6.36	228	9238	3993	185	120	6.02	0.70	0.44	64	0.136	29.2

Table 8.4.15 Descriptive statistics (Median−M, Minimum−Min and Maximum−Max) of BAC (-) for elements through the entire grapevine season (Experiment 3; Milićević et al., 2018b)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sb	Sr	V	Zn
BAC 0-30 cm																					
May																					
M	0.0022	0.0031	0.70	0.0312	0.0019	1.58	0.0034	0.0014	0.0011	0.19	0.0033	0.64	0.15	0.0439	0.07	0.0293	0.0153	0.0013	0.29	0.002376	0.24
Min	0.0008	0.0006	0.22	0.0142	0.0010	0.30	0.0003	0.0007	0.0001	0.06	0.0012	0.33	0.07	0.0120	0.01	0.0002	0.0003	0.0005	0.07	0.000996	0.11
Max	0.0030	0.0081	1.62	0.0660	0.0061	3.69	0.0392	0.0040	0.0059	0.39	0.0064	0.93	0.22	0.1547	0.18	0.0792	0.0892	0.1913	1.17	0.003799	0.46
June																					
M	0.0009	0.0028	1.04	0.0479	0.0012	2.72	0.0009	0.0011	0.0006	0.19	0.0027	0.70	0.25	0.0366	0.17	0.0137	0.0069	0.0019	0.51	0.000910	0.29
Min	0.0006	0.0011	0.67	0.0237	0.0000	0.50	0.0002	0.0008	0.0003	0.13	0.0023	0.62	0.22	0.0171	0.01	0.0002	0.0005	0.0009	0.25	0.000016	0.20
Max	0.0012	0.0062	1.58	0.1023	0.0077	4.19	0.0750	0.0016	0.0013	0.31	0.0031	0.98	0.28	0.2157	0.25	0.0318	0.1758	0.0048	0.98	0.001466	0.38
July																					
M	0.0014	0.0069	0.77	0.0569	0.0014	3.23	0.0012	0.0029	0.0028	0.12	0.0031	0.73	0.26	0.0546	0.14	0.0166	0.0288	0.0052	0.76	0.001734	0.17
Min	0.0010	0.0024	0.46	0.0281	0.0003	0.37	0.0000	0.0013	0.0018	0.04	0.0020	0.50	0.12	0.0096	0.04	0.0002	0.0079	0.0009	0.24	0.000826	0.11
Max	0.0019	0.0156	1.39	0.1117	0.0086	4.94	0.0057	0.0079	0.0142	0.28	0.0082	1.21	0.41	0.2291	0.21	0.0719	0.0647	0.0740	1.18	0.006401	0.24
August																					
M	0.0007	0.0057	0.46	0.0699	0.0012	3.58	0.0005	0.0028	0.0014	0.10	0.0025	0.61	0.31	0.0521	0.07	0.0146	0.0103	0.0026	1.00	0.000805	0.18
Min	0.0003	0.0021	0.31	0.0339	0.0001	0.81	0.0001	0.0012	0.0004	0.06	0.0013	0.40	0.16	0.0196	0.01	0.0002	0.0008	0.0008	0.42	0.000001	0.12
Max	0.0012	0.0244	1.12	0.1312	0.0093	5.88	0.0028	0.0090	0.0230	0.13	0.0051	0.85	0.49	0.1650	0.15	0.0655	0.0448	0.1482	1.50	0.002072	0.33
BAC 30-60 cm																					
May																					
M	0.0022	0.0026	1.30	0.0261	0.0021	1.73	0.0269	0.0016	0.0010	0.20	0.0030	0.71	0.16	0.0462	0.06	0.0269	0.0107	0.0009	0.14	0.001402	0.29
Min	0.0015	0.0010	0.22	0.0120	0.0012	0.11	0.0018	0.0008	0.0001	0.07	0.0018	0.55	0.11	0.0151	0.01	0.0001	0.0002	0.0004	0.03	0.000565	0.16
Max	0.0035	0.0073	2.83	0.0547	0.0064	4.21	0.3384	0.0048	0.0057	0.36	0.0061	1.37	0.23	0.2271	0.19	0.0683	0.0423	0.1150	0.75	0.002249	0.53
June																					
M	0.0010	0.0028	2.32	0.0506	0.0013	2.84	0.0065	0.0014	0.0005	0.22	0.0028	0.98	0.24	0.0400	0.16	0.0112	0.0040	0.0012	0.27	0.000506	0.33
Min	0.0006	0.0009	1.02	0.0243	0.0000	0.14	0.0012	0.0008	0.0003	0.08	0.0024	0.67	0.22	0.0215	0.02	0.0002	0.0003	0.0004	0.10	0.000009	0.18
Max	0.0023	0.0054	3.59	0.0826	0.0085	4.25	0.5260	0.0021	0.0013	0.34	0.0046	1.26	0.35	0.2040	0.28	0.0201	0.0964	0.0031	0.51	0.001114	0.41
July																					
M	0.0014	0.0063	0.84	0.0446	0.0012	3.33	0.0036	0.0031	0.0024	0.13	0.0029	0.78	0.25	0.0590	0.12	0.0137	0.0149	0.0126	0.51	0.001425	0.16
Min	0.0009	0.0023	0.51	0.0251	0.0002	0.19	0.0001	0.0006	0.0013	0.05	0.0019	0.53	0.13	0.0200	0.04	0.0002	0.0045	0.0005	0.13	0.000308	0.10
Max	0.0020	0.0133	2.62	0.0866	0.0085	5.46	0.0231	0.0095	0.0250	0.26	0.0091	1.21	0.37	0.2474	0.23	0.0637	0.0402	0.2974	1.21	0.006954	0.23
August																					
M	0.0007	0.0049	0.50	0.0621	0.0012	4.10	0.0020	0.0030	0.0015	0.12	0.0024	0.77	0.31	0.0498	0.07	0.0125	0.0075	0.0020	0.89	0.000561	0.20
Min	0.0003	0.0018	0.26	0.0215	0.0001	0.29	0.0003	0.0016	0.0002	0.06	0.0012	0.42	0.16	0.0227	0.01	0.0008	0.0004	0.0005	0.15	0.000001	0.11
Max	0.0061	0.0859	1.68	0.1169	0.0098	6.63	0.0108	0.0095	0.0201	0.16	0.0222	3.40	0.50	0.2208	0.15	0.0549	0.0238	0.1022	1.33	0.052076	0.33

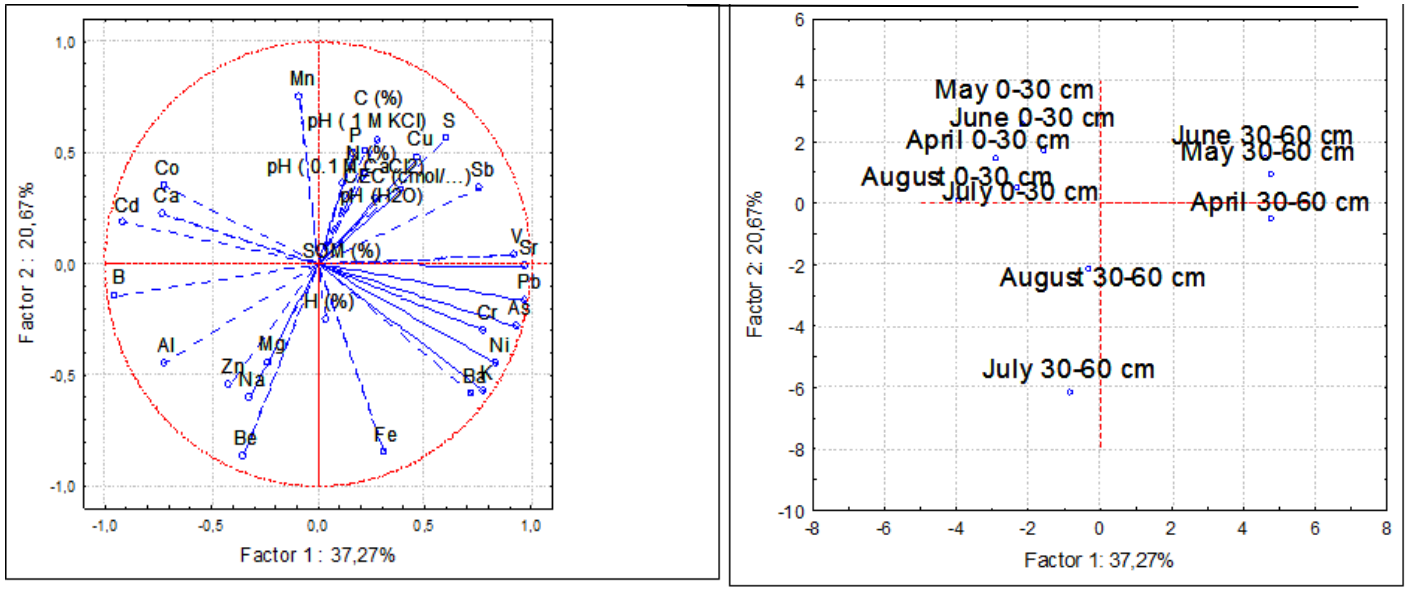


Figure8.4.1 a) PCA representing the relations between the element concentrations (mg kg^{-1}) and physicochemical parameters pH (-), SOM (%), CEC (cmol kg^{-1}), N (%), C (%), H (%) and b) PCA Q-Q plot representing differences between the sampling phases (-) through the season (Experiment 3; Milićević et al., 2018b).

Figure 8.4.2 Eri (-) distribution through the season calculated for both soil layers for a) As; b) Cd; c) Cr; d) Cu; e) Ni; f) Pb; g) Zn and h) RI (-) for the vineyard soil distribution through the season (Experiment 3; Milićević et al., 2018b).

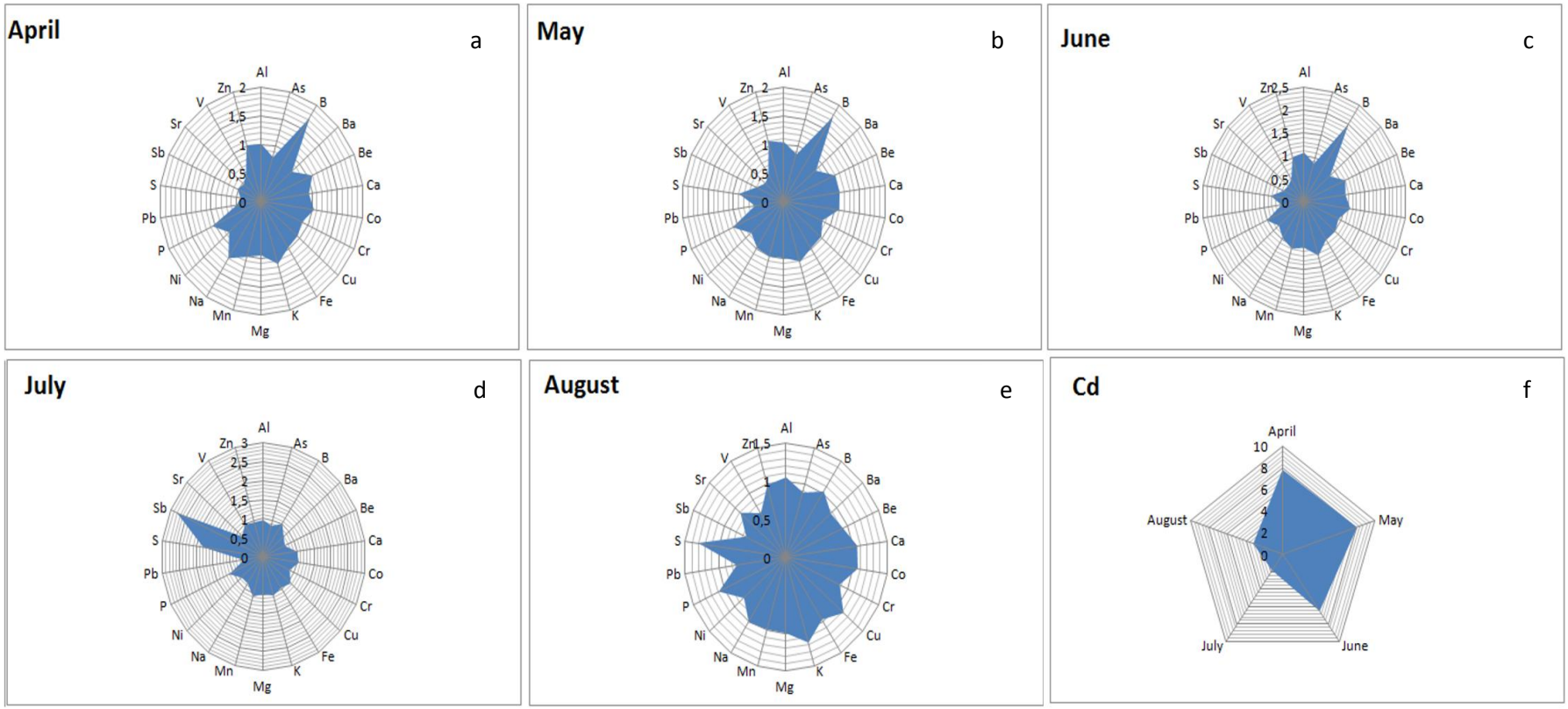


Figure 8.4.3 BGI (-) representing the element absorption in the topsoil through the season a) April; b) May; c) June; d) July; e) August; and f) BGI (-) for Cd through the season. (Experiment 3; Milićević et al., 2018b).

8.5 Appendix 5: Experiment 4

Table 8.5.1 Descriptive statistics (Mean, Median, Minimum, Maximum, Standard Deviation–SD) of the element concentrations (mg kg^{-1}) in the unexposed (Initial) and exposed *S. girgensohnii* and *H. cupressiforme* for three consecutive periods of 2 months (1M2, 2M2 and 3M2), 4 months (M4), and 6 months (M6); RAF – median values of relative accumulation factor (Experiment 4; Milićević et al., 2017b)

S. girgensohnii																						
Element	Initial		1M2				2M2				3M2				M4				M6			
	Mean	SD	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*
Al	286	7	726	414	943	*1.5*	611	475	1000	*1.1*	550	362	3076	*0.9*	832	529	1084	*1.9*	1446	1052	1933	*4.1*
As	0.06	0.03	0.29	0.16	0.5	*3.8*	0.27	0.16	0.46	*3.5*	0.21	0.14	0.61	*2.5*	0.35	0.17	0.51	*4.8*	0.6	0.4	0.95	*9.0*
Ba	27	2	32	26	46	*0.2*	45	32	63	*0.7*	41	30	53	*0.5*	40	31	51	*0.5*	48	42	65	*0.8*
Ca	3196	296	4945	3585	7127	*0.5*	7251	4915	8250	*1.3*	5730	4152	7404	*0.8*	6710	4541	7770	*1.1*	7778	5210	9177	*1.4*
Cd	0.15	0.002	0.21	0.17	0.36	*0.4*	0.372	0.181	0.758	*1.5*	0.290	0.192	0.498	*0.9*	0.284	0.186	0.508	*0.9*	0.297	0.223	0.63	*1.0*
Ce	0.28	0.1	0.52	0.27	0.86	*0.9*	0.87	0.56	1.68	*2.1*	0.78	0.35	2.44	*1.8*	1.44	0.83	1.9	*4.1*	2.53	1.8	3.63	*8.0*
Co	0.4	0.03	0.52	0.39	0.87	*0.3*	0.53	0.35	0.73	*0.3*	0.48	0.24	1.24	*0.2*	0.7	0.54	0.96	*0.8*	0.81	0.54	1.00	*1.0*
Cr	0.18	0.04	1.29	0.48	5.15	*6.2*	1.43	0.76	5.87	*6.9*	1.40	0.56	17	*6.8*	1.97	1.03	11	*9.9*	3.9	2.2	17.8	*20.7*
Cu	2.9	0.4	25	4.4	582	*7.6*	13	4.4	80	*3.5*	10.0	5.7	38	*2.4*	20.7	7.1	197	*6.1*	27.3	15.2	173	*8.4*
Dy	0.006	0.002	0.05	0.03	0.07	*7.3*	0.04	0.02	0.08	*5.7*	0.04	0.01	0.16	*5.7*	0.07	0.03	0.09	*10.7*	0.14	0.1	0.18	*22.3*
Er	0.0037	0.0004	0.02	0.01	0.04	*4.4*	0.02	0.01	0.04	*4.4*	0.02	0.01	0.08	*4.4*	0.03	0.02	0.04	*7.1*	0.07	0.05	0.09	*17.9*
Eu	0.0031	0.001	0.01	0.01	0.02	*2.2*	0.01	0.01	0.03	*2.2*	0.01	0.005	0.05	*2.2*	0.02	0.01	0.03	*5.5*	0.04	0.03	0.06	*11.9*
Fe	344	35	728	459	964	*1.1*	750	618	1170	*1.2*	658	468	2374	*0.9*	961	581	1637	*1.8*	1682	1177	2479	*3.9*
Ga	0.047	0.006	0.2	0.09	0.31	*3.3*	0.29	0.15	0.47	*5.2*	0.22	0.07	0.89	*3.7*	0.34	0.17	0.44	*6.2*	0.65	0.48	0.87	*12.8*
Gd	0.006	0.004	0.06	0.03	0.1	*9.0*	0.04	0.02	0.1	*5.7*	0.05	0.02	0.21	*7.3*	0.09	0.04	0.11	*14.0*	0.17	0.12	0.24	*27.3*
Ho	0.001	0.001	0.009	0.005	0.014	*8.0*	0.006	0.003	0.013	*5.0*	0.007	0.002	0.032	*6.0*	0.012	0.006	0.017	*11.0*	0.025	0.019	0.034	*24.0*
La	0.16	0.03	0.41	0.22	0.66	*1.6*	0.4	0.24	0.78	*1.5*	0.33	0.13	1.14	*1.1*	0.71	0.42	0.92	*3.4*	1.21	0.84	1.74	*6.6*
Li	0.003	0.001	0.051	0.0003	0.209	*16.0*	0.03	0.021	0.06	*9.0*	0.024	0.01	0.208	*7.0*	0.049	0.027	0.17	*15.3*	0.0074	0.0054	0.104	*1.5*
Lu	0.001	0.001	0.0027	0.00155	0.00408	*1.7*	0.0007	0.00003	0.00238	*-0.3*	0.00038	0.00004	0.00761	*-0.6*	0.00423	0.00226	0.00605	*3.2*	0.00757	0.00542	0.01048	*6.6*
Mg	1270	53	1540	1329	1710	*0.2*	1554	710	1960	*0.2*	1584	666	3314	*0.2*	1629	1277	1964	*0.3*	1617	907	3092	*0.3*
Mn	217	19	316	217	957	*0.5*	626	256	1155	*1.9*	375	232	747	*0.7*	436	225	853	*1.0*	408	178	724	*0.9*
Nd	0.05	0.03	0.37	0.18	0.61	*6.4*	0.3	0.18	0.66	*5.0*	0.30	0.13	1.14	*5.0*	0.54	0.3	0.75	*9.8*	1.03	0.73	1.46	*19.6*
Ni	1.1	0.1	3.3	1.7	150	*2.0*	1.3	0.4	4.6	*0.2*	2.1	1	9.4	*0.9*	2.5	1.3	6	*1.3*	3.4	2.5	5.3	*2.1*
Pb	4.3	0.3	4.8	3.5	6.8	*0.1*	5.0	3.7	28	*0.2*	5.1	4.1	7	*0.2*	5.8	4.2	8.8	*0.3*	7.7	5.3	8.7	*0.8*
Pr	0.016	0.008	0.1	0.05	0.16	*5.3*	0.08	0.05	0.17	*4.0*	0.08	0.04	0.29	*4.0*	0.14	0.07	0.2	*7.8*	0.27	0.19	0.4	*15.9*
Sb	0.04	0.01	0.13	0.08	0.24	*2.3*	0.17	0.1	0.28	*3.3*	0.14	0.09	0.32	*2.5*	0.19	0.14	0.91	*3.8*	0.26	0.15	0.61	*5.5*
Sc	0.04	0.03	0.11	0.05	0.16	*1.8*	0.12	0.02	0.23	*2.0*	0.05	0.01	0.52	*0.3*	0.16	0.08	0.29	*3.0*	0.26	0.19	0.44	*5.5*
Sm	0.007	0.005	0.07	0.04	0.12	*9.0*	0.05	0.03	0.12	*6.1*	0.06	0.02	0.23	*7.6*	0.1	0.05	0.14	*13.3*	0.2	0.14	0.29	*27.6*
Sn	0.02	0.01	0.18	0.03	0.31	*8.0*	0.22	0.06	0.47	*10.0*	0.15	0.06	0.41	*6.5*	0.24	0.1	0.4	*11.0*	0.36	0.17	0.87	*17.0*
Sr	7.1	0.7	15	9	23	*1.1*	17	12	21	*1.4*	15	11	18	*1.1*	16	9.5	20	*1.3*	19	13	22	*1.7*
Tb	0.004	0.003	0.0088	0.0044	0.0141	*1.2*	0.0017	0.0001	0.0117	*-0.6*	0.0026	0.0001	0.045	*-0.4*	0.0137	0.009	0.0306	*2.4*	0.02	0.0105	0.038	*4.0*
Th	0.0107	0.0001	0.08	0.04	0.14	*6.5*	0.08	0.05	0.18	*6.5*	0.07	0.03	0.34	*5.5*	0.14	0.07	0.19	*12.1*	0.26	0.17	0.36	*23.3*
Ti	5.4	0.7	15	5	20	*1.8*	24	14	37	*3.4*	22	9	61	*3.1*	38	15	58	*6.0*	70	51	95	*12.0*
Tm	0.0006	0.0002	0.004	0.002	0.013	*5.7*	0.003	0.001	0.006	*4.0*	0.003	0.002	0.012	*4.0*	0.005	0.003	0.022	*7.3*	0.01	0.008	0.019	*15.7*
V	0.5	0.1	1.3	0.7	1.7	*1.6*	1.3	0.9	2.1	*1.6*	1.1	0.7	4.9	*1.2*	1.8	1.1	2.4	*2.6*	3.0	2.2	4.1	*5.0*
Y	0.055	0.008	0.24	0.13	0.35	*3.4*	0.21	0.12	0.38	*2.8*	0.21	0.1	0.84	*2.8*	0.33	0.18	0.44	*5.0*	0.67	0.46	0.9	*11.2*
Yb	0.003	0.001	0.02	0.01	0.03	*5.7*	0.01	0.01	0.03	*2.3*	0.02	0.01	0.06	*5.7*	0.03	0.01	0.04	*9.0*	0.05	0.04	0.07	*15.7*
Zn	25	5	40	28	595	*0.7*	61	30	203	*1.2*	52	28	206	*1.1*	49	29	164	*1.0*	72	40	293	*1.8*

H. cupressiforme

	Initial		1M2				2M2				3M2				M4				M6			
Element	Mean	SD	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*	Median	Min	Max	*RAF*
Al	547	30	878	669	1349	*0.6*	844	622	1019	*0.5*	845	713	1228	*0.5*	1225	898	1836	*1.2*	1524	1016	2166	*1.8*
As	0.15	0.02	0.52	0.37	0.72	*2.5*	0.42	0.26	0.57	*1.8*	0.37	0.24	0.57	*1.5*	0.53	0.30	0.87	*2.5*	0.72	0.37	1.13	*3.8*
Ba	21	1	22	19	25	*0.0*	26	20	34	*0.2*	25	21	37	*0.2*	28	26	41	*0.3*	34	29	42	*0.6*
Ca	5176	190	6073	5332	6865	*0.2*	6862	5569	7427	*0.3*	6472	5276	9135	*0.3*	7406	6515	8659	*0.4*	7244	5056	8594	*0.4*
Cd	0.2	0.1	0.317	0.245	0.491	*0.6*	0.298	0.234	0.407	*0.5*	0.279	0.225	0.414	*0.4*	0.335	0.270	0.555	*0.7*	0.288	0.217	0.391	*0.4*
Ce	1.1	0.1	1.06	0.72	1.76	*0.0*	1.66	1.22	2.23	*0.5*	1.34	1.06	2.51	*0.2*	2.50	1.66	4.29	*1.3*	3.18	1.92	4.67	*1.9*
Co	0.26	0.03	0.53	0.33	0.76	*1.0*	0.41	0.26	0.54	*0.6*	0.4	0.34	0.57	*0.5*	0.64	0.46	1.23	*1.5*	0.71	0.42	0.99	*1.7*
Cr	0.67	0.1	1.8	1.2	6.2	*1.7*	1.7	1.0	5.5	*1.5*	1.8	1.3	3.5	*1.7*	2.52	1.54	11.8	*2.8*	2.9	1.6	14.5	*3.3*
Cu	4.3	0.7	45	11	165	*9.5*	6.6	4.3	42	*0.5*	9.6	6.6	21	*1.2*	23	8.9	161	*4.3*	25	14	205	*4.8*
Dy	0.058	0.001	0.11	0.07	0.19	*0.9*	0.09	0.06	0.13	*0.6*	0.08	0.07	0.16	*0.4*	0.14	0.10	0.27	*1.4*	0.17	0.11	0.25	*1.9*
Er	0.0274	0.0002	0.05	0.03	0.09	*0.8*	0.04	0.03	0.07	*0.5*	0.04	0.03	0.08	*0.5*	0.06	0.04	0.13	*1.2*	0.08	0.05	0.12	*1.9*
Eu	0.012	0.001	0.03	0.02	0.05	*1.5*	0.02	0.02	0.03	*0.7*	0.02	0.02	0.03	*0.7*	0.03	0.02	0.06	*1.5*	0.05	0.03	0.07	*3.2*
Fe	471	4	839	607	1196	*0.8*	857	573	1193	*0.8*	788	623	1022	*0.7*	1163	757	2137	*1.5*	1407	856	2458	*2.0*
Ga	0.27	0.03	0.39	0.27	0.58	*0.4*	0.48	0.38	0.64	*0.8*	0.38	0.29	0.65	*0.4*	0.66	0.47	0.26	*1.4*	0.70	0.45	1.14	*1.6*
Gd	0.0064	0.0002	0.14	0.09	0.23	*20.9*	0.11	0.08	0.16	*16.2*	0.10	0.08	0.18	*14.6*	0.16	0.10	0.32	*24.0*	0.21	0.13	0.31	*31.8*
Ho	0.01	0.0003	0.02	0.01	0.04	*1.0*	0.02	0.01	0.02	*1.0*	0.02	0.01	0.03	*1.0*	0.02	0.02	0.05	*1.0*	0.03	0.02	0.05	*2.0*
La	0.5	0.03	0.78	0.53	1.29	*0.6*	0.74	0.53	0.99	*0.5*	0.58	0.43	1.21	*0.2*	1.15	0.77	2.00	*1.3*	1.41	0.86	2.11	*1.8*
Li	0.02	0.01	0.05	0.0003	0.21	*1.5*	0.04	0.03	0.10	*1.0*	0.04	0.03	0.10	*1.0*	0.07	0.05	0.15	*2.5*	0.07	0.05	0.23	*2.5*
Lu	0.0032	0.0003	0.010	0.0035	0.010	*2.1*	0.004	0.002	0.008	*0.3*	0.002	0.001	0.007	*-0.4*	0.008	0.004	0.014	*1.5*	0.01	0.005	0.01	*2.1*
Mg	1349	64	1427	1244	1645	*0.1*	1450	1164	1582	*0.1*	1468	1229	2403	*0.1*	1480	1264	1701	*0.1*	1486	1108	2843	*0.1*
Mn	70	9	92	71	137	*0.3*	96	77	474	*0.4*	97	68	470	*0.4*	171	77	547	*1.4*	168	76	348	*1.4*
Nd	0.36	0.01	0.77	0.49	1.23	*1.1*	0.64	0.43	0.87	*0.8*	0.58	0.43	0.98	*0.6*	0.95	0.62	1.76	*1.6*	1.21	0.75	1.84	*2.4*
Ni	0.8	0.3	5.7	1.4	36	*6.1*	1.3	0.2	9.6	*0.6*	4.5	1.9	23	*4.6*	2.7	1.5	5.3	*2.4*	3.1	1.3	6.9	*2.9*
Pb	2.0	0.4	5.12	3.58	8.06	*1.6*	3.48	2.47	4.93	*0.7*	4.29	3.3	9.35	*1.1*	5.3	3.8	7.0	*1.7*	5.09	3.07	6.64	*1.5*
Pr	0.096	0.003	0.20	0.13	0.33	*1.1*	0.16	0.12	0.24	*0.7*	0.14	0.11	0.26	*0.5*	0.24	0.16	0.45	*1.5*	0.33	0.19	0.49	*2.4*
Sb	0.04	0.03	0.11	0.06	0.19	*1.8*	0.13	0.07	0.37	*2.3*	0.12	0.07	0.34	*2.0*	0.18	0.10	0.30	*3.5*	0.17	0.01	0.37	*3.3*
Sc	0.044	0.02	0.16	0.11	0.24	*2.6*	0.14	0.08	0.20	*2.2*	0.10	0.04	0.19	*1.3*	0.25	0.13	0.37	*4.7*	0.29	0.17	0.53	*5.6*
Sm	0.0758	0.004	0.16	0.10	0.26	*1.1*	0.12	0.08	0.18	*0.6*	0.11	0.08	0.19	*0.5*	0.19	0.12	0.35	*1.5*	0.24	0.15	0.36	*2.2*
Sn	0.1	0.2	0.13	0.02	0.29	*0.3*	0.21	0.04	0.44	*1.1*	0.16	0.04	0.82	*0.6*	0.23	0.08	0.48	*1.3*	0.29	0.07	0.59	*1.9*
Sr	19	0.8	21	18	24	*0.1*	21	17	24	*0.1*	22	15	28	*0.2*	25	23	29	*0.3*	23	16	29	*0.2*
Tb	0.0063	0.0002	0.02	0.01	0.03	*2.2*	0.01	0.01	0.02	*0.6*	0.01	0.01	0.02	*0.6*	0.02	0.02	0.05	*2.2*	0.03	0.02	0.08	*3.8*
Th	0.11	0.02	0.17	0.11	0.33	*0.5*	0.18	0.14	0.25	*0.6*	0.15	0.11	0.29	*0.4*	0.27	0.17	0.45	*1.5*	0.32	0.19	0.51	*1.9*
Ti	25	3	20	9	34	*-0.2*	39	25	50	*0.6*	35	26	64	*0.4*	56	33	76	*1.2*	71	51	99	*1.8*
Tm	0.004	0.002	0.007	0.005	0.012	*0.8*	0.006	0.004	0.009	*0.5*	0.006	0.005	0.011	*0.5*	0.009	0.005	0.017	*1.3*	0.012	0.007	0.017	*2.0*
V	1.1	0.02	1.99	1.56	2.97	*0.8*	1.99	1.59	2.56	*0.8*	1.8	1.4	2.37	*0.6*	2.63	1.9	3.63	*1.4*	3.0	2.1	4.5	*1.7*
Y	0.30	0.02	0.55	0.36	0.94	*0.8*	0.47	0.33	0.70	*0.6*	0.41	0.32	0.87	*0.4*	0.67	0.44	1.31	*1.2*	0.86	0.56	1.17	*1.9*
Yb	0.0022	0.0004	0.04	0.03	0.07	*17.2*	0.03	0.02	0.05	*12.6*	0.03	0.03	0.06	*12.6*	0.05	0.03	0.10	*21.7*	0.07	0.04	0.1	*30.8*
Zn	19	1	40	24	132	*1.1*	29	24	73	*0.47*	30	23	91	*0.6*	34	26	63	*0.8*	35	22	79	*2.6*

Table 8.5.2 Spearman's correlation coefficients ($p < 0.05$) between the element concentrations within the studied moss species (*S. girgensohnii* and *H. cupressiforme*) exposed for 2, 4 and 6 months (Experiment 4; Milićević et al., 2017b)

		S.g. Al	*H.c.* Al	*S.g.* As	*H.c.* As	*S.g.* Ba	*H.c.* Ba	*S.g.* Ca	*H.c.* Ca	*S.g.* Cd	*H.c.* Cd	*S.g.* Co	*H.c.* Co	*S.g.* Cr	*H.c.* Cr	*S.g.* Cu	*H.c.* Cu	*S.g.* Fe	*H.c.* Fe	*S.g.* Li	*H.c.* Li	*S.g.* Mg	*H.c.* Mg	*S.g.* Mn	*H.c.* Mn	*S.g.* Ni	*H.c.* Ni	*S.g.* Pb	*H.c.* Pb	*S.g.* Sb	*H.c.* Sb	*S.g.* Sn	*H.c.* Sn	*S.g.* Sr	*H.c.* Sr	*S.g.* Ti	*H.c.* Ti	*S.g.* V	*H.c.* V	*S.g.* Zn	*H.c.* Zn
		Al	Al	As	As	Ba	Ba	Ca	Ca	Cd	Cd	Co	Co	Cr	Cr	Cu	Cu	Fe	Fe	Li	Li	Mg	Mg	Mn	Mn	Ni	Ni	Pb	Pb	Sb	Sb	Sn	Sn	Sr	Sr	Ti	Ti	V	V	Zn	Zn
S.g.	Al	1.00																																					
H.c.	Al	**0.56**	1.00																																				
S.g.	As	**0.90**	0.55	1.00																																			
H.c.	As	0.46	0.75	0.47	1.00																																		
S.g.	Ba	**0.52**	0.22	0.37	0.11	1.00																																	
H.c.	Ba	0.41	0.70	0.36	0.38	0.26	1.00																																
S.g.	Ca	**0.61**	0.30	0.47	0.20	**0.78**	0.31	1.00																															
H.c.	Ca	0.28	0.55	0.23	0.28	0.17	0.70	0.23	1.00																														
S.g.	Cd	0.28	0.02	0.12	-0.04	**0.80**	-0.01	**0.61**	0.07	1.00																													
H.c.	Cd	-0.06	0.17	0.00	0.20	-0.27	0.10	-0.20	0.21	-0.13	1.00																												
S.g.	Co	**0.80**	0.55	**0.75**	0.32	0.40	0.53	**0.57**	0.28	0.12	-0.06	1.00																											
H.c.	Co	**0.51**	0.86	**0.53**	0.76	0.07	0.51	0.14	0.39	-0.01	0.42	0.44	1.00																										
S.g.	Cr	**0.72**	0.44	**0.64**	0.33	**0.59**	0.37	**0.58**	0.19	0.40	-0.23	**0.68**	0.36	1.00																									
H.c.	Cr	0.37	0.66	0.35	0.56	0.28	0.49	0.27	0.32	0.10	-0.06	0.41	0.56	**0.70**	1.00																								
S.g.	Cu	0.41	0.17	0.36	0.24	0.17	-0.11	0.22	-0.10	0.23	0.20	0.28	0.33	0.20	-0.01	1.00																							
H.c.	Cu	0.40	0.49	0.37	0.50	-0.16	0.24	0.02	0.14	-0.21	0.31	0.39	0.60	0.21	0.26	**0.56**	1.00																						
S.g.	Fe	**0.94**	0.52	**0.84**	0.42	**0.65**	0.46	**0.69**	0.29	0.35	-0.15	**0.79**	0.43	**0.82**	0.48	0.29	0.25	1.00																					
H.c.	Fe	**0.54**	0.93	**0.52**	0.74	0.32	0.69	0.37	0.55	0.08	0.09	**0.55**	0.80	**0.56**	0.81	0.11	0.37	**0.57**	1.00																				
S.g.	Li	**0.73**	0.39	**0.76**	0.34	0.34	0.24	0.39	0.16	0.15	-0.01	**0.63**	0.37	0.50	0.21	0.41	0.33	**0.66**	0.33	1.00																			
H.c.	Li	0.41	0.76	0.43	0.69	0.02	0.40	0.11	0.34	-0.14	0.30	0.36	0.78	0.19	0.39	0.24	0.52	0.31	0.69	0.34	1.00																		
S.g.	Mg	0.17	0.14	0.18	0.07	-0.10	0.31	-0.10	0.18	-0.37	-0.12	0.37	0.08	0.14	0.11	-0.05	0.21	0.17	0.15	0.07	0.08	1.00																	
H.c.	Mg	0.02	0.25	0.05	0.05	0.03	0.12	0.19	0.11	0.04	-0.26	0.06	0.09	0.12	0.17	-0.21	-0.12	0.06	0.23	-0.05	0.07	-0.25	1.00																
S.g.	Mn	0.05	-0.07	-0.09	-0.06	**0.63**	-0.14	0.44	-0.06	**0.62**	-0.16	0.05	-0.14	0.20	0.10	0.10	-0.22	0.14	0.04	-0.06	-0.13	-0.12	-0.15	1.00															
H.c.	Mn	0.19	0.49	0.21	0.28	0.04	0.70	0.04	0.49	-0.19	0.39	0.28	0.49	0.03	0.22	-0.10	0.23	0.19	0.45	0.10	0.37	0.23	-0.11	-0.09	1.00														
S.g.	Ni	**0.55**	0.32	**0.55**	0.36	0.11	0.11	0.16	-0.01	-0.04	-0.05	**0.54**	0.36	0.44	0.25	0.34	0.49	0.48	0.27	0.48	0.26	0.16	0.06	-0.16	-0.04	1.00													
H.c.	Ni	0.10	0.10	0.06	0.18	-0.02	0.00	-0.12	-0.20	0.04	0.00	0.11	0.17	0.21	0.19	0.25	0.37	0.06	0.05	-0.07	-0.04	0.04	0.03	-0.01	-0.03	0.39	1.00												
S.g.	Pb	**0.64**	0.40	**0.61**	0.33	0.45	0.40	0.45	0.21	0.22	-0.02	**0.58**	0.34	**0.52**	0.22	0.27	0.27	**0.66**	0.37	0.48	0.32	0.24	-0.04	0.03	0.19	0.30	0.06	1.00											
H.c.	Pb	0.12	0.58	0.15	0.61	-0.25	0.23	-0.24	0.14	-0.21	0.35	0.10	0.70	0.04	0.36	0.16	0.56	0.02	0.51	0.11	0.58	0.08	0.12	-0.22	0.28	0.29	0.35	0.05	1.00										
S.g.	Sb	**0.65**	0.54	**0.69**	0.39	0.37	0.50	**0.52**	0.46	0.21	0.09	**0.56**	0.46	0.47	0.26	0.13	0.19	**0.64**	0.49	**0.52**	0.35	0.12	0.15	-0.10	0.29	0.29	0.00	**0.62**	0.18	1.00									
H.c.	Sb	0.35	0.61	0.33	0.49	0.17	0.55	0.35	0.57	0.15	0.17	0.29	0.53	0.27	0.42	-0.02	0.15	0.34	0.61	0.28	0.46	0.03	0.16	-0.14	0.29	-0.01	-0.13	0.38	0.34	**0.63**	1.00								
S.g.	Sn	**0.76**	0.48	**0.71**	0.37	0.43	0.38	**0.59**	0.39	0.32	0.01	**0.61**	0.44	0.49	0.16	0.36	0.32	**0.70**	0.42	**0.59**	0.41	0.12	0.08	0.07	0.13	0.34	-0.01	**0.63**	0.06	**0.71**	0.46	1.00							
H.c.	Sn	0.22	0.57	0.20	0.35	0.19	0.64	0.35	0.55	0.11	0.10	0.34	0.40	0.24	0.41	-0.12	0.15	0.25	0.54	0.17	0.36	0.09	0.21	0.04	0.39	-0.06	-0.01	0.26	0.24	0.39	0.56	0.33	1.00						
S.g.	Sr	**0.51**	0.18	0.38	0.20	**0.71**	0.06	**0.73**	-0.02	**0.56**	-0.18	0.43	0.07	0.47	0.20	0.25	0.07	**0.55**	0.25	0.26	0.12	-0.01	-0.03	**0.59**	-0.05	0.22	0.12	0.37	-0.14	0.27	-0.01	0.42	0.14	1.00					
H.c.	Sr	0.18	0.43	0.13	0.14	0.01	0.62	0.05	0.83	-0.05	0.19	0.22	0.31	0.13	0.22	-0.10	0.16	0.15	0.37	0.10	0.24	0.20	0.15	-0.14	0.42	0.04	-0.14	0.13	0.11	0.30	0.37	0.18	0.45	-0.18	1.00				
S.g.	Ti	**0.81**	0.58	**0.70**	0.30	**0.64**	0.65	**0.67**	0.49	0.42	-0.13	**0.71**	0.40	**0.69**	0.38	0.18	0.14	**0.82**	0.56	**0.58**	0.30	0.17	0.15	0.12	0.31	0.25	-0.03	**0.62**	-0.02	**0.68**	0.50	**0.76**	0.47	0.37	0.39	1.00			
H.c.	Ti	0.48	0.78	0.46	0.44	0.46	0.79	0.48	0.57	0.23	0.02	**0.55**	0.53	0.45	0.54	0.03	0.15	**0.54**	0.75	0.33	0.45	0.17	0.22	0.13	0.50	0.05	-0.02	0.43	0.19	**0.57**	0.58	**0.50**	0.73	0.25	0.43	**0.76**	1.00		
S.g.	V	**0.96**	0.57	**0.86**	0.43	**0.60**	0.49	**0.69**	0.33	0.35	-0.10	**0.82**	0.48	**0.75**	0.38	0.36	0.34	**0.93**	0.56	**0.70**	0.39	0.19	0.05	0.12	0.22	0.48	0.06	**0.67**	0.08	**0.69**	0.39	**0.80**	0.31	**0.51**	0.21	**0.88**	0.59	1.00	
H.c.	V	**0.55**	0.95	**0.55**	0.81	0.19	0.66	0.30	0.58	-0.01	0.25	0.48	0.86	0.35	0.60	0.16	0.48	**0.50**	0.91	0.40	0.80	0.11	0.17	-0.09	0.50	0.25	-0.02	0.40	0.56	**0.55**	0.67	**0.51**	0.57	0.14	0.40	**0.54**	0.73	**0.55**	1.00
S.g.	Zn	0.33	0.01	0.22	0.10	**0.68**	-0.09	0.48	0.02	**0.79**	-0.11	0.14	0.05	0.40	0.10	0.41	-0.06	0.37	0.08	0.22	-0.09	-0.19	-0.15	**0.55**	-0.27	0.19	0.17	0.24	-0.14	0.21	0.06	0.38	-0.05	0.49	-0.12	0.33	0.13	0.35	0.00
H.c.	Zn	0.14	0.26	0.09	0.27	-0.06	0.33	0.04	0.10	-0.11	0.22	0.21	0.35	0.18	0.30	0.19	0.51	0.11	0.29	-0.04	0.16	0.00	-0.03	-0.02	0.41	0.21	0.58	0.13	0.36	0.02	0.01	0.08	0.27	0.14	0.13	0.05	0.13	0.12	0.24

Table 8.5.3 Spearman's correlation coefficients ($p<0.01$) between the REE concentrations in the studied moss species exposed for 2, 4 and 6 months (Experiment 4; Milićević et al., 2017b)

S. girgensohnii

	Ce	Dy	Er	Eu	Ga	Gd	Ho	La	Lu	Nd	Pr	Sc	Sm	Tb	Th	Tm	Y	Yb
Ce	1.00																	
Dy	0.79	1.00																
Er	0.80	0.99	1.00															
Eu	0.84	0.98	0.97	1.00														
Ga	0.93	0.85	0.84	0.88	1.00													
Gd	0.79	0.99	0.99	0.98	0.84	1.00												
Ho	0.78	0.98	0.99	0.97	0.82	0.98	1.00											
La	0.89	0.95	0.95	0.97	0.92	0.95	0.94	1.00										
Lu	0.72	0.92	0.92	0.90	0.74	0.91	0.92	0.90	1.00									
Nd	0.84	0.98	0.98	0.99	0.89	0.99	0.97	0.97	0.89	1.00								
Pr	0.84	0.98	0.98	0.99	0.89	0.99	0.98	0.97	0.89	1.00	1.00							
Sc	0.82	0.85	0.85	0.88	0.90	0.85	0.83	0.92	0.83	0.87	0.87	1.00						
Sm	0.82	0.99	0.98	0.99	0.87	0.99	0.98	0.96	0.90	0.99	0.99	0.86	1.00					
Tb	0.71	0.89	0.89	0.89	0.71	0.90	0.90	0.89	0.96	0.88	0.88	0.84	0.89	1.00				
Th	0.90	0.96	0.95	0.97	0.93	0.95	0.95	0.98	0.87	0.98	0.98	0.90	0.97	0.85	1.00			
Tm	0.73	0.85	0.86	0.84	0.73	0.85	0.85	0.84	0.84	0.85	0.85	0.79	0.84	0.83	0.84	1.00		
Y	0.83	0.99	0.99	0.98	0.88	0.98	0.98	0.96	0.90	0.99	0.99	0.86	0.98	0.88	0.97	0.84	1.00	
Yb	0.82	0.98	0.99	0.97	0.85	0.98	0.98	0.95	0.92	0.98	0.98	0.85	0.98	0.89	0.96	0.86	0.99	1.00

H. cupressiforme

	Ce	Dy	Er	Eu	Ga	Gd	Ho	La	Lu	Nd	Pr	Sc	Sm	Tb	Th	Tm	Y	Yb
Ce	1.00																	
Dy	0.77	1.00																
Er	0.78	0.99	1.00															
Eu	0.78	0.96	0.96	1.00														
Ga	0.94	0.81	0.81	0.81	1.00													
Gd	0.77	0.99	0.98	0.97	0.80	1.00												
Ho	0.77	0.99	0.98	0.95	0.80	0.98	1.00											
La	0.87	0.96	0.96	0.97	0.89	0.96	0.94	1.00										
Lu	0.72	0.94	0.94	0.94	0.77	0.94	0.92	0.93	1.00									
Nd	0.80	0.98	0.98	0.98	0.83	0.99	0.97	0.98	0.92	1.00								
Pr	0.82	0.98	0.98	0.98	0.85	0.99	0.97	0.98	0.93	1.00	1.00							
Sc	0.71	0.76	0.76	0.81	0.72	0.78	0.74	0.83	0.82	0.79	0.80	1.00						
Sm	0.78	0.98	0.98	0.98	0.80	0.99	0.97	0.97	0.93	0.99	0.99	0.79	1.00					
Tb	0.71	0.94	0.94	0.94	0.75	0.95	0.92	0.94	0.96	0.94	0.94	0.85	0.95	1.00				
Th	0.90	0.89	0.90	0.90	0.92	0.89	0.89	0.95	0.85	0.92	0.93	0.80	0.90	0.84	1.00			
Tm	0.78	0.97	0.97	0.94	0.80	0.96	0.97	0.94	0.91	0.96	0.95	0.74	0.95	0.91	0.88	1.00		
Y	0.79	0.99	0.99	0.96	0.83	0.99	0.98	0.96	0.93	0.98	0.98	0.75	0.98	0.93	0.91	0.97	1.00	
Yb	0.78	0.98	0.98	0.95	0.81	0.98	0.98	0.94	0.92	0.97	0.97	0.76	0.97	0.92	0.90	0.97	0.98	1.00

8.6 Appendix 6: Experiment 5

Table 8.6.1 Descriptive statistics (Median–M, Minimum–Min, Maximum–Max and Standard Deviation–SD) of pseudo-total element concentrations (mg kg^{-1}) in the soil samples

	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sb	Si	Sr	V	Zn
Organic soil layer O (0-5 cm)																										
M	57061	19	64	316	3.4	0.27	66075	0.17	18	123	29	33206	2234	25	9775	771	23002	90	629	40	198	0.32	2487	145	80	84
Min	47246	16	43	279	3.1	0.24	33389	0.14	18	102	23	31373	2031	22	7857	635	15682	66	416	36	44	0.28	1901	97	70	73
Max	74121	23	1319	393	3.8	0.35	107325	0.24	22	138	49	38273	2967	35	12333	993	68647	123	1342	50	314	0.39	5781	224	95	103
SD	9359	3	590	41	0.2	0.03	23481	0.03	2	13	8	2165	262	4	1576	121	22744	18	273	4	88	0.04	1520	49	6	8
Topsoil A (0-30 cm)																										
M	63524	22	47	290	3.3	0.27	64910	0.17	19	119	36	33445	1778	31	9635	783	11725	101	401	41	111	0.29	847	144	73	85
Min	49800	16	25	152	2.3	0.22	36565	0.15	17	84	23	26383	892	23	7546	562	5523	74	328	28	7	0.15	347	64	49	60
Max	73534	24	1176	447	4.1	0.35	114405	0.23	23	147	73	38663	2625	37	11110	980	52657	119	735	57	317	0.45	4604	248	93	95
SD	7024	3	292	81	0.4	0.04	25931	0.02	2	16	13	3297	486	4	1260	145	18458	15	136	7	99	0.08	1528	53	11	10
Subsoil/Control sample (30-60 cm)																										
M	71968	23	44	222	3.1	0.24	77552	0.24	20	118	37	32905	1610	42	9252	710	10060	119	401	36	58	0.22	714	121	70	81
Min	56214	16	36	192	2.5	0.23	30355	0.14	17	90	22	27416	1354	29	7107	636	9233	103	297	30	19	0.19	566	87	56	63
Max	77306	25	51	314	3.6	0.32	109346	0.56	21	128	43	37819	2133	44	9792	970	15259	142	500	44	164	0.31	748	214	84	94
SD	8894	4	5	49	0.5	0.04	29536	0.17	2	16	8	4430	308	7	1080	152	2441	15	78	6	63	0.05	83	48	11	12
*MAC								3		100	100							50		100						300

Table 8.6.2 Spearman's correlation analysis between the element concentrations obtained in the soil samples

	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sb	Si	Sr	V	Zn
Al																										
As	0.75																									
B																										
Ba		0.56																								
Be		0.63		0.84																						
Bi		0.55			0.67																					
Ca						-0.66																				
Cd						0.89	-0.50																			
Co		0.54			0.58	0.74	-0.69	0.56																		
Cr	0.52	0.90		0.76	0.79	0.61	-0.23		0.52																	
Cu						0.82	-0.59	0.82																		
Fe		0.52			0.76	0.88	-0.82	0.72	0.78	0.55	0.76															
K		0.66		0.91	0.82	0.51	-0.30			0.88																
Li	0.87	0.61				0.68	-0.44	0.67	0.61		0.53	0.73														
Mg		0.69				0.61	-0.25		0.58	0.76			0.70													
Mn						0.84	-0.67	0.82	0.77		0.77	0.85		0.62												
Na				0.90	0.60					0.65			0.82													
Ni	0.64													0.63												
P			0.54			0.86		0.84	0.60		0.64	0.68		0.60	0.59	0.77										
Pb		0.64		0.86	0.95	0.69	-0.54	0.53	0.57	0.87		0.65	0.88		0.60		0.69		0.52						
S			0.54			0.76		0.78			0.67	0.56		0.63	0.53	0.64		0.53	0.92							
Sb		0.56		0.99	0.84					0.76			0.91				0.90			0.86		1.00				
Si			0.53	0.79									0.73				0.92			0.56		0.79	1.00			
Sr		0.57													0.60		0.38					0.22	0.25	1.00		
V		0.65		0.86	0.95	0.68	-0.62	0.47	0.60	0.84		0.73	0.92		0.67		0.65		0.54	0.93		0.86	0.56	0.16	1.00	
Zn		0.53		0.54	0.76	0.89	-0.81	0.67	0.80	0.56	0.67	0.90	0.63	0.66	0.57	0.72			0.76	0.69	0.67	0.54	0.13	-0.10	0.74	1

p<0.01

p<0.05

Table 8.6.3 Descriptive statistics (Median–M, Minimum–Min, Maximum–Max and Standard Deviation–SD) of the element concentrations (mg kg^{-1}) extracted from the soil samples using deionised H_2O procedures and Mobility factor (MF%)

	deionised H_2O 2h					deionised H_2O 16 h				
	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%
Al	1.93	1.8	1.96	0.03	0.00013	1.93	1.77	1.99	0.04	0.0001
As	8.5	1.8	41	8	/	5.18	2.61	21.03	3.6	/
B		<DL		/	/		<DL		/	/
Ba	0.5	0.3	1.1	0.2	0.002	0.43	0.14	0.92	0.19	0.0016
Be	0.002	0.0004	0.005	0.001	0.00047	0.00145	0.00003	0.00303	0.00074	0.0004
Ca	290	191	711	141	0.0057	394	141	666	114	0.0069
Cd	0.0008	0.0003	0.0026	0.0003	0.0046	0.0008	0.0006	0.0014	0.0002	0.0046
Co	0.0054	0.0009	0.0262	0.006	0.00037	0.0036	0.0001	0.0168	0.004	0.0004
Cr	0.028	0.007	0.224	0.04	0.00027	0.022	0.008	0.053	0.009	0.0002
Cu	0.24	0.01	0.67	0.2	0.004	0.14	0	0.98	0.25	0.002
Fe	3.88	0.86	25.94	5.5	0.00012	2.42	0.38	13.2	2.28	0.0001
K	15	5	128	30	0.00638	13	4	140	34	0.0059
Li	0.044	0.009	0.079	0.03	0.001	0.038	0.007	0.091	0.028	0.0009
Mg	20	9	68	14	0.0028	25	11	58	13	0.0031
Mn	0.34	0.17	1.29	0.3	0.00042	0.36	0.09	1.15	0.25	0.0004
Mo		<DL		/	/		<DL		/	/
Na	8.7	1.2	86.4	20.5	0.0006	9.5	2.7	102.3	23	0.0009
Ni	0.07	0.02	0.2	0.05	0.0007	0.06	0.01	0.17	0.05	0.0006
P	2.06	0.8	17.6	3.4	0.006	1.76	0.5	16.21	3.36	0.0036
Pb	0.06	0.004	0.52	0.09	0.001	0.05	0.01	0.12	0.03	0.0011
S	6.63	1.45	29.2	6.4	0.04	6.28	0.01	31.83	6.64	0.0414
Sb		<DL		/	/		<DL		/	/
Si		<DL		/	/		<DL		/	/
Sr	0.75	0.4	2.2	0.46	0.0045	0.94	0.44	2.04	0.42	0.0053
V	0.02	0.01	0.1	0.02	0.00032	0.02	0.01	0.06	0.01	0.0002
Zn	0.01	0	2.67	0.79	0.00002	0.501	0.001	4.413	1.433	0.0077

Table 8.6.4 Descriptive statistics (Median–M, Minimum–Min, Maximum–Max and Standard Deviation–SD) of the element concentrations (mg kg^{-1}) extracted from the soil samples using different weak salt solutions as single extraction procedures and Mobility factor (MF%)

	0.01 mol L^{-1} $CaCl_2$					*0.1 mol L^{-1} $BaCl_2$*					*1 mol L^{-1} NH_4NO_3*					*1 mol L^{-1} $NaNO_3$*				
	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%
Al	2.48	1.02	8.64	1.52	0.00005	0.18	0.06	0.79	0.14	0.000003	3.89	0.01	12.74	2.85	0.0001	1.29	0.15	5.28	1.23	0.00002
As		<DL		/	/		<DL		/	/		<DL		/	/		<DL		/	/
B		<DL		/	/	0.21	0.01	2.68	0.61	0.0045		<DL		/	/	0.59	0.01	8.33	2.12	0.004
Ba	2.15	1.52	3.14	0.44	0.00813		<DL		/	/	30	25	41	5	1.4		<DL		/	/
Be		<DL		/	/		<DL		/	/		<DL		/	0.0004		<DL		/	0.0008
Ca			/			6094	4805	7626	704	0.12	3814	3169	5387	444	0.91	867	704	1014	78	0.014
Cd	0.001	0.00002	0.0011	0.0004	0.004	0.004	0.0002	0.007	0.003	0.018		<DL		/	/	0.006	0.002	0.042	0.01	0.033
Co		<DL		/	0.00009	0.0097	0.00001	0.041	0.011	0.0006		<DL		/	/	0.008	0.008	0.092	0.023	0.0005
Cr	0.004	0.001	0.03	0.007	0.00003		<DL		/	/	0.015	0.003	0.029	0.007	0.0001	0.005	0.001	0.091	0.016	0.00005
Cu		<DL		/	/		<DL		/	/	0.16	0.04	0.28	0.08	0.0047	0.12	0.01	3.5	0.8	0.003
Fe	0.02	0.02	4.96	1.03	0.000001		<DL		/	/	2.92	0.33	7.84	1.85	0.0001	0.99	0.01	4.52	1.11	0.00005
K	39	12	297	69	0.022	76	11	614	149	0.0357	109	25	567	123	0.76	0.02	0.02	81.91	17.75	0.00001
Li	0.07	0.017	0.13	0.04	0.0015	0.12	0.04	0.19	0.05	0.0025	0.12	0.05	0.19	0.05	0.004	0.045	0.012	0.074	0.021	0.001
Mg	178	82	350	79	0.02	403	171	651	135	0.0399	231	111	458	106	0.36	61	30	127	28	0.006
Mn	0.26	0.08	0.93	0.23	0.00036	0.58	0.07	0.99	0.2	0.0005	0.46	0.17	1.78	0.41	0.0007	0.17	0.05	0.86	0.22	0.0002
Mo		<DL		/	/		<DL		/	/		<DL		/	/		<DL		/	/
Na	13.1	3.7	141	32.1	0.00098	11.6	4	138	32.7	0.001	12.4	3.6	113.3	26.8	0.0005	/				
Ni	1.89	0.01	0.18	0.05	0.00045		<DL		/	/	0.06	0.02	0.13	0.03	0.0007	0.02	0.01	0.09	0.03	0.0002
P	0.77	0.22	5.42	1.34	0.0023		<DL		/	/	0.83	0.18	5.25	1.15	0.002	0.35	0.12	4.85	1.01	0.0011
Pb		<DL		/	/		<DL		/	/	0.011	0.008	0.034	0.005	0.0003	0.14	0.05	1.03	0.3	0.0031
S	5.97	0.07	32.4	6.46	0.054		<DL		/	/	6.43	2.97	21.68	4.43	0.055	2.75	0.16	15.61	3.63	0.018
Sb		<DL		/	/		<DL		/	/		<DL		/	/		<DL		/	/
Si		<DL		/	/		<DL		/	/		<DL		/	0.028	3.86	2.22	7.85	1.38	0.0029
Sr	7.39	4.02	13.1	2.52	0.047	23.7	12.2	30.9	7.4	0.12	13.3	8.1	23	4.7	1.4	2.89	1.76	5.21	0.97	0.019
V	0.02	0.01	0.05	0.01	0.0003		<DL		/	/	0.009	0.009	0.031	0.006	0.0001	0.02	0.02	0.07	0.01	0.00032
Zn	0.54	0.001	5.94	1.15	0.006		<DL		/	/	0.091	0.0007	0.79	0.18	0.0007	0.0000001	0.0000001	1.63	0.31	0.00003

Table 8.6.5 Descriptive statistics (Median–M, Mean, Minimum–Min, Maximum–Max and Standard Deviation–SD) of the element concentrations (mg kg^{-1}) extracted from the soil samples using different weak acid solution and complexing agent as single extraction procedures and Mobility factor (MF%)

	0.11 mol L^{-1} CH3COOH					*0.44 mol L^{-1} CH3COOH*					*0.5 mol L^{-1} Na2EDTA*				
	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%	M	Min	Max	SD	MF%
Al	0.0133	0.0001	0.0494	0.0136	0.000001	147	110	200	25	0.002	23	12	114	29	0.0003
As		<DL		/	/		<DL		/	/		<DL		/	/
B	1.2	0.002	4.5	1.2	0.01	3.01	0.9	6.19	1.38	0.057	1.44	0.82	9.01	1.9	0.03
Ba	34.3	0.001	148	30.1	0.12	46.9	37.1	60.3	6.8	0.174	3.01	0.67	5.58	1.1	0.01
Be	0.0255	0.0009	0.25	0.06	0.001	0.12	0.07	0.19	0.03	0.035	0.024	0.006	0.075	0.02	0.007
Ca	28292	5483	107718	20906	0.48	3.32	1.24	9.24	2.07	0.0001	18267	16576	20653	952	0.32
Cd	0.047	0.0007	0.16	0.04	0.19	0.08	0.06	0.12	0.01	0.511	0.07	0.03	0.14	0.03	0.37
Co	0.12	0.002	0.59	0.17	0.004	0.38	0.11	1.91	0.41	0.032	0.53	0.12	2.96	0.9	0.036
Cr	0.059	0.002	0.34	0.07	0.0004	0.5	0.26	0.83	0.17	0.004	0.028	0.003	0.074	0.01	0.0002
Cu	0.025	0.002	2.058	0.395	0.0006	0.75	0.39	3	0.55	0.021	6.5	1.01	27.65	6.3	0.16
Fe	5.3	0.002	28	7.41	0.0001	31	23	41	4	0.001	46	18	91	19	0.0014
K	204	0.002	954	229	0.06	201	107	797	164	0.105	6	0.1	236	57	0.0027
Li	1.04	0.0003	8.84	1.82	0.01	0.47	0.26	0.75	0.15	0.013	0.2	0.11	0.3	0.06	0.0054
Mg	1148	20	6354	1166	0.10	1152	480	2436	589	0.144	264	184	566	117	0.033
Mn	70	4	357	66	0.06	117	61	177	33	0.145	65	28	257	65	0.068
Mo		<DL		/	/		<DL		/	/	0.016	0.015	0.04	0.004	/
Na	54.93	0.07	255	48.08	0.004	41.2	19.1	183	39.2	0.004			/		
Ni	1.81	0.06	5.48	1.32	0.01	6.12	2.89	9.26	1.9	0.054	3.08	0.94	12.4	2.9	0.025
P	29	0.02	408	88	0.007	18	0.04	344	78	0.037	0.14	0.14	105.02	19.8	0.0013
Pb	0.029	0.004	0.127	0.027	0.001	0.43	0.15	1.16	0.23	0.01	3.31	2.16	6.78	1.4	0.08
S	24.7	0.07	163	31.35	0.16	22	0.07	69	20	0.14	0.75	0.72	22.4	4.7	0.0056
Sb		<DL		/	/	0.009	0.002	0.097	0.027	0.006	0.07	0.07	0.26	0.06	0.22
Si	232	45	1103	250	0.145	250	244	203	52	0.12	56.2	41.3	98.9	16.2	0.034
Sr	79	18	443	81	0.44	85	31.3	163	38.9	0.6	18.1	11.8	32.7	5.4	0.12
V	0.0133	0.0001	0.0494	0.0136	0.0001	0.11	0.06	0.2	0.03	0.001	0.13	0.02	0.72	0.14	0.0014
Zn	0.3556	0.001	2.1721	0.531	0.0017	0.54	0.06	3.18	1	0.006	1.04	0.01	6.16	1.43	0.014

Table 8.6.6 Descriptive statistics (Median−M, Mean, Minimum-Min, Maximum-Max and Standard Deviation-SD) of the biogeochemical index (BGI) (-) calculated for all measured elements in the soil sample

	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sb	Si	Sr	V	Zn
													BGI O/A													
M	0.90	0.91	1.18	0.95	1.00	0.99	0.93	0.95	0.96	1.00	0.92	0.99	1.03	0.89	0.99	0.98	1.04	0.95	1.38	1.01	1.86	0.95	0.91	0.93	1.02	0.99
Mean	0.99	0.90	14.07	1.01	0.99	0.99	0.92	1.00	0.97	1.01	0.90	0.99	1.25	0.91	1.00	0.99	3.25	0.94	1.42	0.97	2.81	1.01	4.84	0.99	1.06	1.01
Min	0.85	0.76	0.48	0.74	0.87	0.94	0.70	0.88	0.88	0.87	0.67	0.95	0.96	0.81	0.88	0.82	0.34	0.82	1.04	0.79	0.46	0.74	0.44	0.77	0.93	0.94
Max	1.37	1.03	48.32	1.36	1.11	1.05	1.18	1.21	1.06	1.21	1.14	1.05	2.07	1.05	1.17	1.13	11.21	1.04	2.02	1.18	7.89	1.36	12.87	1.51	1.31	1.08
SD	0.17	0.10	17.97	0.26	0.09	0.03	0.15	0.11	0.05	0.11	0.12	0.03	0.38	0.07	0.09	0.09	3.76	0.07	0.26	0.14	2.52	0.26	5.50	0.21	0.12	0.05

Table 8.6.7 Descriptive statistics (Median−M, Minimum-Min, Maximum-Max and Standard Deviation-SD) of CF (-) and PLI (-) calculated for PTEs in the soil sample

	Al	As	B	Ba	Be	Bi	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sr	V	Zn	*PLI*
										CF O layer									
M	0.92	0.91	1.46	1.43	1.10	1.07	0.81	0.96	1.12	1.00	1.06	0.98	0.70	1.16	1.43	1.00	1.24	1.06	*1.02*
Mean	0.91	0.94	14.13	1.38	1.11	1.06	0.76	0.99	1.12	1.01	1.05	0.99	0.74	1.12	1.38	1.12	1.20	1.05	*1.12*
Min	0.61	0.70	1.06	0.90	0.90	0.87	0.24	0.89	0.87	0.72	0.91	0.90	0.60	0.90	0.90	0.80	0.94	0.84	*0.86*
Max	1.14	1.33	32.75	1.58	1.28	1.17	1.39	1.12	1.32	1.32	1.16	1.12	0.89	1.21	1.58	1.86	1.37	1.19	*1.35*
SD	0.18	0.19	15.39	0.22	0.12	0.09	0.36	0.08	0.13	0.18	0.09	0.07	0.11	0.10	0.22	0.33	0.14	0.11	*0.19*
										CF A layer									
M	0.90	0.97	1.00	1.18	1.05	1.03	0.85	0.99	1.03	1.12	1.02	0.99	0.83	1.05	1.18	1.11	1.04	1.00	*1.02*
Mean	0.92	1.02	2.51	1.25	1.07	1.04	0.78	1.00	1.05	1.10	1.03	1.00	0.82	1.09	1.25	1.18	1.07	1.00	*1.02*
Min	0.67	0.78	0.68	0.79	0.90	0.92	0.26	0.90	0.87	0.63	0.91	0.80	0.65	0.91	0.79	0.53	0.87	0.84	*0.88*
Max	1.09	1.38	22.98	1.93	1.36	1.19	1.15	1.16	1.34	1.72	1.17	1.24	0.97	1.49	1.93	1.67	1.43	1.14	*1.19*
SD	0.11	0.17	5.67	0.36	0.15	0.08	0.30	0.06	0.14	0.26	0.09	0.13	0.11	0.19	0.36	0.31	0.15	0.09	*0.09*

Table 8.6.8 Descriptive statistics (Median−M, Minimum−Min, Maximum−Max and Standard Deviation−SD) of the environmental risk calculated for PTEs (ErAs, ErCd, ErCr, ErCu, ErNi, ErPb and ErZn) and total risk (RI) according to concentrations measured in the vineyard soil

	ErAs	ErCd	ErCr	ErCu	ErNi	ErPb	ErZn	RI
				O layer				
M	4.58	24.29	2.21	4.96	3.52	5.76	1.05	44.35
Mean	4.69	23.18	2.20	4.94	3.72	5.52	1.04	45.29
Min	3.49	7.29	1.73	3.58	3.02	4.52	0.84	31.24
Max	6.66	41.73	2.64	6.58	4.47	6.04	1.19	63.80
SD	0.90	10.12	0.26	0.89	0.55	0.50	0.11	9.08
				A layer				
M	4.84	25.61	2.05	5.60	4.17	5.26	1.00	46.95
Mean	5.12	23.35	2.11	5.51	4.10	5.45	1.00	46.63
Min	3.92	7.82	1.74	3.16	3.25	4.56	0.84	31.56
Max	6.91	34.56	2.69	8.59	4.86	7.46	1.14	57.22
SD	0.84	9.13	0.29	1.32	0.55	0.94	0.09	7.83

Table 8.6.9 Descriptive statistics (Median−M, Mean, Minimum−Min, Maximum−Max and Standard Deviation−SD) of bioavailability risk assessment (-) calculated for the soil samples using element concentrations extracted by Na_2EDTA (regular equation); The $BRAI_{probable}$ (using concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn) and $BRAI_{apparent}$ (using concentrations of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn)

	$BRAI_{probable}$	$BRAI_{apparent}$
M	2.94	1.68
Mean	2.96	1.72
Min	1.00	0.84
Max	4.43	2.59
SD	0.76	0.38

Table 8.6.10 Descriptive statistics (Median−M, Mean, Minimum−Min, Maximum−Max and Standard Deviation−SD) of health riks index (non-carcinogenic risk) and carcinogenic risk assessed for the workers in the investigated vineyard

	HIo	HIi	HId	ΣHI	Ro	Ri	Rd	ΣR
M	0.24	0.0049	0.0065	0.25	3.4E-05	7.2E-07	1.47E-06	3.61E-05
Mean	0.24	0.0051	0.0063	0.25	3.26E-05	7.06E-07	1.42E-06	3.47E-05
Min	0.19	0.0043	0.0049	0.20	2.41E-05	5.13E-07	1.09E-06	2.57E-05
Max	0.28	0.0062	0.0077	0.30	4.04E-05	8.87E-07	1.73E-06	4.30E-05
SD	0.02	0.0006	0.0009	0.03	4.08E-06	9.01E-08	2.03E-07	4.36E-06

Table 8.6.11 Descriptive statistics (Median−M, Minimum−Min, Maximum−Max and Standard Deviation−SD) of the element concentrations (mg kg^{-1}) in the grapevine berry and its parts (seed, pulp, skin, whole berry)

	Seed				*Pulp*				*Skin*				*Whole berry*				
	M	Min	Max	SD	M	Min	Max	SD	M	Min	Max	SD	M	Min	Max	SD	MAC
Al	3.6	0.3	6.4	2	5.3	3.6	13.4	3.8	3.9	1.2	37.9	14	1.5	0.3	2.3	1	
As	0.05	0.04	0.07	0.01	0.0191	0.017	0.025	0.003	0.0097	0.004	0.016	0.005	0.00028	0.00025	0.00029	0.00002	0.1
B	11.7	5.8	20.7	6.3	15.7	11.4	20.5	3.7	8.5	7.3	9.6	0.9	3.8	1.1	6.1	1.9	
Ba	2.3	1.7	2.9	0.5	0.6	0.3	0.9	0.2	0.57	0.4	1.04	0.26	0.44	0.25	0.9	0.26	
Be	0.001	0.001	0.0098	0.0036	0.0007	0.0005	0.001	0.0003	0.0005	0.0005	0.001	0.0002	0.0005	0.0005	0.0008	0.0001	
Bi	0.06	0.04	0.20	0.06	0.013	0.008	0.020	0.004	0.00351	0.00013	0.00905	0.00339	0.00013	0.00012	0.09551	0.03894	
Ca	2312	2046	2401	143	734	579	959	147	957	856	1107	85	1495	1130	1810	241	
Cd	0.04	0.037	0.05	0.005	0.013	0.011	0.017	0.002	0.0032	0.003	0.0042	0.0004	0.0002	0.0002	0.0002	0.00001	0.05
Co	0.044	0.036	0.059	0.009	0.019	0.013	0.021	0.003	0.009	0.007	0.012	0.002	0.0001	0.0001	0.0024	0.0009	
Cr	0.05	0.04	0.09	0.02	0.02	0.01	0.03	0.01	0.01	0	0.03	0.01	0.00032	0.00029	0.00033	0.00002	
Cu	5.7	5.1	10.5	2.1	1.7	1.1	2.1	0.4	1.9	1	2.8	0.7	1.4	0.9	2.1	0.5	
Fe	6.2	4.5	7.7	1.1	4.6	2.9	5.8	1	4.7	3.5	7.2	1.4	2.4	2	4.3	0.9	
K	1543	1368	1854	182	10438	3804	20249	6116	5910	4793	11526	2779	7784	4366	12415	2905	
Li	0.007	0.001	0.019	0.008	0.002	0.001	0.009	0.003	0.001	0.001	0.003	0.001	0.00074	0.00065	0.00076	0.00005	
Mg	536	503	700	85	428	352	454	38	507	475	531	23	536	437	638	66	
Mn	7.3	5	9.2	2.1	1.2	0.6	1.8	0.4	2	1.6	2.6	0.4	2.9	1.4	4.6	1.2	
Mo	0.08	0.07	0.12	0.02	0.028	0.026	0.036	0.004	0.017	0.01	0.049	0.016	0	0	0.017	0.007	
Na	100	78	123	16	122	109	156	17	88	71	105	12	8.5	6.1	14.1	3.4	
Ni	0.8	0.1	7.1	2.7	0.05	0	0.38	0.14	0	0	0.61	0.24	0	0	0.31	0.12	
P	1.1	1	1.5	0.2	0.64	0.31	0.75	0.17	0.68	0.6	0.73	0.04	0.92	0.57	1.21	0.23	
Pb	0.99	0.93	1.07	0.05	0.85	0	1.08	0.39	0.3	0.25	1.74	0.59		<DL			1
S		<DL				<DL				<DL				<DL			
Sb	0.0264	0.0236	0.0389	0.0055	0.0108	0.0099	0.0139	0.0016	0.0045	0.0022	0.0053	0.0011	0.00013	0.00010	0.00019	0.00001	
Si		<DL				<DL				<DL				<DL			
Sr	7.6	5.1	10.5	2	1.4	0.4	1.7	0.5	2.2	1.4	3.2	0.6	2	0.8	2.6	0.7	
V	0.023	0.020	0.029	0.003	0.0123	0.008	0.026	0.007	0.009	0.006	0.018	0.004	0.000063	0.000056	0.000065	0.000004	
Zn	15.5	9.3	20.4	3.8	1.32	0	3.17	1.17	1.5	0.7	2.4	0.7	0.0028	0.0024	0.0028	0.0002	

DL-limit of detection

MAC-maximum allowable concentrations in the fresh fruit (Official Gazette of Republic of Serbia, prescribed values for fresh fruit)

Table 8.6.12 Descriptive statistics (Median−M, Minimum–Min, Maximum–Max and Standard Deviation–SD) of the element concentrations (mg kg^{-1}) in the petiole and leaf

	Petiole				*Leaf*			
	M	Min	Max	SD	M	Min	Max	SD
Al	6.7	0.5	9.7	3.9	59	35	260	52
As	0.0006	0.0006	0.0122	0.0036	0.05	0.03	0.14	0.03
B	19	6	22	5	50	26	94	18
Ba	21	10	26	6	9.7	4	30	5.9
Be	0.0021	0.0011	0.0108	0.0038	0.0053	0.0034	0.0309	0.0078
Bi	0.00028	0.00027	0.56824	0.17956	0.0009	0.00082	0.00093	0.00003
Ca	15361	3679	22995	6849	47337	23077	73021	14698
Cd	0.0004	0.0004	0.0154	0.0047	0.0067	0.0008	0.042	0.0133
Co	0.0868	0.0009	0.1929	0.0613	0.042	0.0001	0.1061	0.0328
Cr	0.01	0	0.37	0.13	0.25	0.15	0.89	0.19
Cu	6.1	3.8	14	3.4	9.5	3.9	116	27
Fe	6.4	0.1	9.5	3.1	92	70	197	31
K	10620	4247	28301	7333	12718	7749	24452	4098
Li	0.023	0.002	0.155	0.048	0.005	0.005	0.032	0.008
Mg	3971	773	14731	4723	4501	1845	12763	3110
Mn	26	8	119	37	115	48	264	58
Mo	0.143	0.001	0.633	0.188	0.072	0.011	0.282	0.068
Na	63	28	196	64	23	1	114	43
Ni	0.47	0.01	2.1	0.84	1.85	0.76	4.37	1.08
P	1.21	0.26	2.06	0.53	3505	2572	5848	724
Pb		<DL			0.37	0.22	2.26	0.7
S		<DL			3.5	2.6	5.8	0.7
Sb	0.0002	0.0001	0.003	0.0009	0.03	0.01	0.1	0.02
Si		<DL				<DL		
Sr	67	39	139	32	61	20	135	38
V	0.006	0.0001	0.02	0.01	0.07	0.01	0.46	0.11
Zn	11	0.01	25	7	21	12	57	13

DL–limit of detection

Table 8.6.13 Median−M values of BAC for each element

M	seed/soil	seed/soil	pulp/soil	pulp/soil	skin/soil	skin/soil	berry/soil	berry/soil	petiole/soil	petiole/soil	leaf/soil	leaf/soil
	0-5 cm	0-30 cm	0-5 cm	0-30 cm	0-5 cm	0-30 cm	0-5 cm	0-30 cm	0-5 cm	0-30 cm	0-5 cm	0-30 cm
Al	6.39E-05	5.68E-05	8.5E-05	7.54E-05	6.65E-05	5.73E-05	2.58E-05	4.05E-05	1.40E-04	1.30E-04	0.001	9.00E-04
As	0.0027	0.0023	0.001	8.60E-04	5.20E-04	4.60E-04	1.59E-05	1.18E-05	3.42E-05	2.77E-05	0.042	0.04
B	0.16	0.21	0.25	0.3	0.19	0.16	0.09	0.09	0.33	0.31	1.01	1.07
Ba	0.007	0.006	0.001	0.001	0.002	0.002	0.001	0.0009	0.08	0.064	0.05	0.04
Be	3.00E-04	3.00E-04	2.00E-04	2.00E-04	2.00E-04	1.00E-04	2.00E-04	0.0001	6.00E-04	6.00E-04	0.0011	0.0011
Bi	0.3	0.28	0.047	0.047	0.014	0.014	5.20E-04	0.001	0.001	0.001	0.012	0.013
Ca	0.039	0.036	0.016	0.014	0.014	0.013	0.024	0.026	0.39	0.35	0.86	0.73
Cd	0.26	0.24	0.09	0.082	0.021	0.018	0.0013	0.0011	0.0029	0.0026	0.01	0.01
Co	0.002	0.0024	9.22 E-04	0.000877	0.000438	0.000463	5.54E-06	5.21E-06	0.006	0.006	0.004	0.004
Cr	4.00 E-04	3.47 E-04	1.36 E-04	1.18 E-04	4.45E-05	3.87E-05	2.76E-06	2.32E-06	6.01E-06	5.53E-06	0.0018	0.0017
Cu	0.18	0.16	0.05	0.04	0.05	0.04	0.04	0.04	0.26	0.25	0.15	0.13
Fe	0.000164	1.71 E-04	0.000134	1.27 E-04	1.33 E-04	1.34 E-04	6.89E-05	6.60E-05	2.00 E-04	1.72 E-04	0.003	0.002
K	0.71	0.7	4.01	3.91	2.57	2.57	3.39	2.79	5.72	5.71	6.18	5.92
Li	6.34E-05	5.61E-05	3.28E-05	3.07E-05	3.11E-05	2.86E-05	2.87E-05	2.37E-05	/	/	2.00E-04	2.0 E-04
Mg	0.07	0.06	0.044	0.042	0.055	0.05	0.055	0.052	372	325	0.77	0.68
Mn	0.01	0.01	0.0015	0.0014	0.0026	0.0024	0.0038	0.0034	0.008	0.0071	0.16	0.17
Mo	/	/	/	/	/	/	/	/	2.20E-04	2.20E-04	/	/
Na	0.005	0.002	0.007	0.003	0.004	0.002	3.28 E-04	1.78 E-04	0.004	0.001	2.50 E-04	0.0002
Ni	0.012	0.012	0.001	0.001	2.86E-05	2.57E-05	2.69E-05	2.51E-05	0.0033	0.0033	0.019	0.02
P	0.002	0.003	7.80E-04	0.0012	0.001	0.0016	0.0014	0.0019	0.0019	0.003	6.02	9.61
Pb	0.025	0.022	0.022	0.018	0.007	0.006	/	/	/	/	0.009	0.008
S	/	/	/	/	/	/	/	/	8.22E-07	/	0.021	0.025
Sb	0.085	0.067	0.035	0.029	0.015	0.011	2.34 E-04	01.73 E-04	0.02	0.013	0.061	0.051
Sr	0.049	0.044	0.007	0.006	0.013	0.012	0.009	0.008	0.63	0.57	0.6	0.54
V	2.98 E-04	2.93 E-04	1.44 E-04	1.34 E-04	8.63E-05	8.17E-05	7.6E-07	7.04E-07	6.13E-05	5.72E-05	7.23E-04	6.84 E-04
Zn	0.17	0.16	0.01	0.01	0.02	0.02	3.06E-05	3.01E-05	0.15	0.15	0.18	0.17

Table 8.6.14 Median−M values of RF

RF (M)	RF leaf/pulp	RF leaf/seed	RF skin/pulp	RF skin/seed	RF petiole/pulp	RF petiole/seed
Al	12	24	0.6	1.56	0.68	1.88
As	2.28	0.77	0.33	0.23	0.03	0.01
B	2.78	4.95	0.45	0.72	1.02	1.19
Ba	14	3.3	1.02	0.26	43	11.21
Be	17.3	16.5	0.95	0.49	2.28	1.08
Bi	0.07	0.01	0.27	0.05	0.02	0
Ca	40	13	1.29	0.42	26	8.34
Cd	1.81	0.61	0.23	0.08	0.03	0.01
Co	0.04	0.02	0.48	0.2	7.84	2.89
Cr	0.15	0.05	0.35	0.12	0.06	0.02
Cu	10	3.18	1.25	0.26	4.68	1.22
Fe	0.01	0.01	0.98	0.61	22	16
K	1.55	9.11	0.55	3.62	1.85	8.06
Mg	0.001	0.001	1.17	0.94	23	19
Mn	3039	517	1.61	0.28	58.75	8.6
Mo	3688	1420	0.58	0.25	7.65	2.79
Na	0.001	0.001	0.71	0.94	0.53	0.73
Ni	4343	125	0.18	0.01	7.9	0.1
Li	786	1223	0.26	0.51	32	25
P	7.78	3.63	1.06	0.62	2.37	1.23
Pb	1.53	1.39	0.34	0.29	/	/
Sb	338	132	0.38	0.16	0.01	0.01
Se	4.34	0.78	0.97	0.07	1.79	0.16
Sr	33	4.3	1.6	0.3	82	10
V	6.28	3.28	0.62	0.35	0.43	0.22
Zn	12.5	1.2	1.8	0.1	14.6	1.1

Table 8.6.15 Descriptive statistics (Median, Mean, Minimum–Min, Maximum–Max and Standard Deviation–SD) of health risk index (non-carcinogenic risk for adults and children) and carcinogenic risk (adjustable) assessed for the grape consumers

	Adults	Children	TR adjustable
	ΣHI	ΣHI	ΣR
parcel 1	0.21	0.29	3.76E-07
parcel 2	0.13	0.17	4.23E-07
parcel 3	0.26	0.35	3.69E-07
parcel 4	0.22	0.32	4.12E-07
parcel 5	0.25	0.38	4.21E-07
M	0.22	0.32	4.12E-07
Min	0.13	0.17	3.69E-07
Max	0.26	0.38	4.23E-07
SD	0.05	0.08	2.5743E-08

Table 8.6.16 Descriptive statistics (Median–M, Mean, Minimum–Min, Maximum–Max and Standard Deviation–SD) of element concentrations (mg kg^{-1}) measured in the moss bags (*Spagnum girgenshonii*) exposed during 2 months (2M) and 4 months (4M) in the organic vineyard and relative accumulation factor (RAF)

	Initial	2M *Sphagnum girghenshonii*						4M *Sphagnum girgenshonii*					
	Mean	M	Mean	Min	Max	SD	*RAF*	M	Mean	Min	Max	SD	*RAF*
Al	89	177	183	149	242	31	*0.99*	263	278	160	377	81	*1.9*
As	0.04	0.08	0.08	0.05	0.11	0.02	*1.3*	0.16	0.14	0.08	0.21	0.04	*3.2*
B	0.47	3	17	2	129	39	*6.3*	1.6	1.8	0.9	3.1	0.7	*2.4*
Ba	7.53	14	14	8	23	5	*0.81*	14	14	9	16	3	*0.84*
Be	0.004	0	0.01	0	0.02	0.01	*0.11*	0.01	0.01	0	0.03	0.01	*0.41*
Bi	0.001	0.001	0.077	0.001	0.759	0.24	*0.1*	0.001	0.001	0.001	0.001	0.0001	*0.11*
Ca	5028	6364	6490	5594	7924	816	*0.27*	7285	7542	5983	9261	1011	*0.45*
Cd	0.06	0.16	0.15	0.07	0.3	0.07	*1.7*	0.12	0.12	0.08	0.19	0.03	*1.01*
Co	0.07	0.15	0.16	0.12	0.25	0.04	*1.19*	0.22	0.22	0.16	0.29	0.05	*2.31*
Cr	0.16	0.57	0.55	0.4	0.8	0.13	*2.58*	0.71	0.72	0.4	1.09	0.25	*3.45*
Cu	2.06	3.48	3.88	2.47	6.05	1.28	*0.69*	3.01	4.09	1.33	8.24	2.19	*0.46*
Fe	88	194	198	164	261	29	*1.21*	329	380	190	570	147	*2.75*
K	15221	5083	5250	2200	7837	1847	*-0.67*	2308	2753	1211	5012	1545	*-0.85*
Li	0.003	0.001	0.01	0.001	0.05	0.02	*0.89*	0	0.01	0	0.04	0.02	*0.91*
Mg	2317	2289	2236	1668	2773	300	*-0.01*	2886	2866	2590	3183	208	*0.25*
Mn	361	452	482	365	680	110	*0.25*	511	525	395	671	91	*0.42*
Mo	0.11	0.12	0.13	0.09	0.26	0.05	*0.11*	0.09	0.1	0.07	0.14	0.02	*-0.14*
Na	73	50	56	35	113	24	*-0.31*	43	48	34	75	13	*-0.4*
Ni	2.03	1.35	2.41	0.56	9.96	2.89	*-0.34*	2.33	3.49	0.9	10.16	3.2	*0.15*
P	2.41	0.97	0.97	0.91	1.05	0.05	*-0.6*	0.88	0.88	0.8	0.96	0.05	*-0.63*
Pb	0.8	1.14	1.15	0.87	1.5	0.18	*0.43*	1.62	1.94	1.03	4.29	0.99	*1.03*
S	2.41	0.97	0.97	0.91	1.05	0.05	*-0.6*	0.88	0.88	0.8	0.96	0.05	*-0.63*
Sb	0.02	0.07	0.14	0.05	0.5	0.16	*2.59*	0.1	0.18	0.07	0.57	0.17	*4.4*
Sr	5.78	9.1	9.87	6.52	17.78	3.39	*0.57*	9.39	8.96	5.64	10.6	1.71	*0.63*
V	0.22	0.61	0.61	0.47	0.86	0.12	*1.76*	0.89	0.86	0.51	1.2	0.27	*3*
Zn	12	50	58	19	132	38	*3.02*	31	34	17	65	17	*1.6*

8.7 Appendix 7: Experiment 6

Table 8.7.1 Descriptive statistics (Median–M, Minimum–Min and Maximum–Max) of the total element concentrations (mg kg^{-1}) measured by non-destructive analytical method wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) and magnetic parameters saturation isothermal remanent magnetisation (SIRM) ($x10^{-6}$ A m^2 kg^{-1}) and magnetic susceptibility (χ) (m^3 kg^{-1}) obtained in the soil samples from commercial and organic vineyards

	Al	Ba	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Rb	S	Si	Sr	Ti	V	Zn	Zr	SIRM	χ
Commercial vineyard																								
April																								
M	63600	447	8055	58	266	49	45800	15550	8144	1085	3045	169	453	46	117	118	279650	92	5195	132	104	386	1219	2.50E-07
Min	59200	374	5060	47	151	37	43800	14100	6570	737	1770	99	236	39	102	46	231700	66	4380	125	94	267	806	1.63E-07
Max	67100	529	44600	75	352	141	51100	17500	10300	1330	3690	284	677	49	142	177	289900	162	5720	147	113	484	4929	4.79E-05
May																								
M	62267	475	6850	60	281	47	45800	15000	7400	1180	3240	167	549	45	118	117	282000	90	5450	131	107	445	1417	2.39E-07
Min	50800	387	4680	52	156	40	43000	14000	6610	965	1810	97	377	33	103	75	218800	63	4300	117	93	272	733	1.64E-07
Max	67800	530	49100	71	625	175	50300	17200	8990	1590	4040	292	916	61	142	233	298400	177	6000	143	130	508	6454	3.13E-03
June																								
M	58400	459	7295	58	269	46	45650	14750	6965	1205	3210	166	472	49	124	106	280650	93	5430	129	100	459	1401	2.16E-07
Min	49500	390	5090	49	168	41	43500	13500	6290	948	2550	99	372	41	103	91	213600	87	4680	121	92	302	841	1.56E-07
Max	66100	616	51400	66	491	83	48800	17500	7740	1930	3560	218	638	59	137	150	288400	182	5630	138	111	501	7987	1.50E-04
July																								
M	62550	457	6945	58	265	46	46650	15000	7855	1145	3165	167	514	41	117	123	278100	90	5275	133	101	421	1484	2.46E-07
Min	59100	385	5210	43	172	33	42100	12500	6470	968	1730	96	355	35	104	91	209800	67	4330	115	88	258	916	1.64E-07
Max	71900	581	69700	70	428	162	52700	17400	10200	1650	4000	311	713	108	137	160	298400	170	5960	145	115	508	9735	1.42E-04
August																								
M	59900	462	8270	56	270	48	46200	14700	7270	1170	3340	169	474	49	119	114	276700	91	5120	129	102	416	1866	2.23E-07
Min	52200	390	5130	41	194	32	42300	13200	6460	1010	1620	95	348	40	103	82	219600	62	4210	119	92	257	721	1.58E-07
Max	63400	521	49300	72	399	101	51700	17400	8970	1510	4040	304	727	99	135	160	290600	183	5800	142	115	496	5948	1.10E-04
Organic vineyard																								
June																								
M	59450	464	84000	56	184	61	43650	14000	9235	827	1850	174	480	ND	94	129	193600	189	4205	118	102	223	1576	2.51E-07
Min	41700	381	37200	40	152	28	33000	9160	7800	762	1650	130	362	ND	68	44	127000	159	3340	83	74	172	501	7.17E-08
Max	69500	568	157300	64	259	81	54500	17700	10400	1290	2130	203	601	ND	150	219	228600	306	4890	144	125	269	1664	1.11E-04
July																								
M	57100	475	70150	55	187	59	43400	14300	9295	862	1815	176	622	ND	103	152	192100	260	4130	120	112	202	1849	2.96E-07
Min	53600	376	38500	48	156	46	40500	11600	8160	781	1510	118	404	ND	72	96	162500	141	3610	109	82	164	845	3.25E-08
Max	64800	576	119600	62	215	134	50600	19000	11000	1210	2820	216	1560	ND	139	295	238400	314	4830	137	132	345	2191	3.50E-03
September																								
M	59300	485	72050	56	182	59	44500	15150	9245	819	2000	160	564	ND	107	203	196100	198	4165	119	103	228	1838	7.83E-05
Min	51000	376	34400	50	164	39	39200	10600	7550	644	1640	131	340	ND	77	89	159700	151	3740	95	90	162	873	1.63E-07
Max	67100	531	115600	59	232	106	51000	17600	10400	1170	2950	198	917	ND	145	284	242300	321	4800	131	125	350	2271	1.30E-04

ND–not detected concentration by Uniquant WD-XRF

Table 8.7.2 Descriptive statistics (Median–M, Minimum–Min and Maximum–Max) of the total element concentrations (mg kg^{-1}) measured by nondestructive analytical method wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) and two magnetic parameters saturation isothermal remanent magnetisation (SIRM) ($\times 10^{-6}$ A m^2 kg^{-1}) and magnetic susceptibility (χ) (m^3 kg^{-1}) obtained in the leaf samples from commercial and organic vineyards

	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	P	Rb	S	Si	Sr	Ti	Zn	SIRM	χ
Commercial vineyard																		
May																		
M	491	21800	27	256	18400	2730	151	971	6.5	7730	21	4460	1540	41	12	60	38	-3.50E-09
Min	396	18000	17	146	13800	2150	71	784	5.7	5500	6	3980	871	15	4.5	41	22	-4.70E-08
Max	663	25300	51	287	24000	3660	765	1640	9.9	9850	52	5210	2150	56	19	90	80	3.17E-08
June																		
M	151	26950	14	155	14550	2985	76	793.5	ND	3565	8.9	2430	2875	46	3.6	38	39	-3.9E-09
Min	120	21400	8.7	113	12200	2210	60	572	ND	2900	3.9	1770	1620	30	2.8	28	31	-1.90E-08
Max	201	30200	30	186	22500	3900	448	975	ND	6120	20	3510	4190	72	10	45	88	3.28E-08
July																		
M	204	26800	9	124	12500	3170	91	752	4.9	2860	9.3	2190	4170	53	8.1	22	47	5.84E-09
Min	164	22200	4.5	87	8330	2290	31	566	4.8	2030	6.3	1520	2230	21	3.5	15	26	-3.80E-08
Max	352	29000	18	442	18900	4510	418	978	5	3840	20	3080	6860	70	12	29	202	2.84E-08
August																		
M	135	29300	4.2	94	9020	2750	72	554	4.15	1930	8.35	1500	5030	54	3.9	16	53	2.55E-09
Min	74	26300	2.1	58	5210	2140	32	417	2.8	1390	4.8	1170	3000	24	2	9.3	29	-2.80E-07
Max	205	33400	8.8	253	15700	3850	277	722	5.7	3250	18	1830	8590	86	9.3	29	146	1.68E-08
Organic vineyard																		
June																		
M	235	27000	36	200	16100	3410	132	818	ND	3500	17	2640	2490	107	8.5	24	58	-2.2E-08
Min	127	25400	12	150	9860	3090	93	700	ND	2510	10	2360	1710	46	4.1	21	44	-9.1E-07
Max	353	30000	83	229	17000	3930	180	963	ND	3920	19	2860	3280	116	10	53	69	3.1E-09
July																		
M	205	31100	41	137	8120	2730	140	598	2.8	1920	9.55	1430	3940	110	7.95	19	97	9.31E-09
Min	152	29100	6.8	117	5640	382	119	500	2.8	1730	6.1	1230	3330	62	5.6	13	71	-5.00E-07
Max	305	31700	113	156	10200	4140	164	966	2.8	2180	13	1580	6310	151	28	44	168	2.27E-08
August																		
M	156	27800	5.9	133	8300	4920	110	664	ND	2520	12	1450	3750	99	5.85	15	153	1.12E-08
Min	139	22800	3.2	104	5650	1250	68	569	ND	2290	6	1300	2090	80	3.9	14	132	-4.40E-08
Max	194	31000	19	178	15300	6680	277	683	ND	3840	25	2360	4000	158	11	27	265	3.54E-08

ND–not detected concentrations

Table 8.7.3 Ratio (%) between the element concentrations obtained by non-destructive (WD-XRF) and destructive (ICP-OES and ICP-MS) methods

Soil pseudo total *vs.* total content																		
	Al	Ba	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sr	V	Zn
%	111.1	53.5	99.6	42.0	54.4	88.9	90.6	68.5	115.6	91.2	23.8	63.4	72.9	40.1	83.2	47.5	50.5	79.9
Leaf destructive *versus* nondestructive total content																		
	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Zn								
%	36.1	91.4	68.3	80.7	49.7	76.9	68.9	10.4	61.7	67.7								

Figure 8.7.4: Correlation between the element concentrations obtained by ICP-OES and WD-XRF (pseudo-total (destructive) *versus* total element content (nondestructive) in the soil samples from the vineyards

	Al_ICP	Ba_ICP	Ca_ICP	Co_ICP	Cr_ICP	Cu_ICP	Fe_ICP	K_ICP	Mg_ICP	Mn_ICP	Na_ICP	Ni_ICP	P_ICP	Pb_ICP	S_ICP	Sr_ICP	V_ICP	Zn_ICP
Al_XRF	**0.40****																	
Ba_XRF		**0.40***																
Ca_XRF			**0.99****															
Co_XRF				**0.40****														
Cr_XRF					**0.60****													
Cu_XRF						**0.77****												
Fe_XRF							**0.50****											
K_XRF								**0.40****										
Mg_XRF									**0.63****									
Mn_XRF										**0.62****								
Na_XRF											**-0.46****							
Ni_XRF												**0.86****						
P_XRF													**0.87****					
Pb_XRF														-0.1				
S_XRF															**0.78****			
Sr_XRF																**0.98****		
V_XRF																	0.01	
Zn_XRF																		**0.40****

** Correlation is significant at the 0.01 level (2-tailed).

Figure 8.7.5 Correlation between the element concentrations obtained by ICP-OES and WD-XRF (destructive *vs.* nondestructive) in the leaf samples from the vineyards

	Al_ICP	Ca_ICP	Cu_ICP	Fe_ICP	K_ICP	Mg_ICP	Mn_ICP	Na_ICP	Sr_ICP	Zn_ICP
Al_XRF	**0.85****									
Ca_XRF		**0.68****								
Cu_XRF			**0.83****							
Fe_XRF				**0.52****						
K_XRF					**0.40****					
Mg_XRF						0.14				
Mn_XRF							0.03			
Na_XRF								-0.16		
Sr_XRF									**0.40****	
Zn_XRF										-0.16

** Correlation is significant at the 0.01 level (2-tailed).

8.7.6 Spearman's correlations (R) between the magnetic parameters and element concentrations in the soil samples from the commercial and the organic vineyards obtained by ICP-OES and WD-XRF

	Commercial			Organic	
R	SIRM	χ		SIRM	χ
Al_ICP	-0.40**	-0.20	Al_ICP	0.17	0.23
As_ICP	0.40**	0.40**	As_ICP	0.06	0.19
B_ICP	0.22*	0.30*	B_ICP	0.07	0.21
Ba_ICP	-0.60**	-0.42**	Ba_ICP	0.39	0.40
Be_ICP	-0.30**	-0.16	Be_ICP	0.33	0.73**
Ca_ICP	0.71**	0.60**	Bi_ICP	0.41*	0.80**
Cd_ICP	0.15	0.16	Ca_ICP	-0.65**	-0.86**
Co_ICP	0.07	0.12	Cd_ICP	0.07	0.60**
Cr_ICP	0.30**	0.22*	Co_ICP	0.60**	0.80**
Cu_ICP	0.01	-0.02	Cr_ICP	0.24	0.37
Fe _ICP	0.06	0.16	Cu_ICP	0.30	0.80**
K_ICP	0.18	0.23*	Fe_ICP	0.60**	0.90**
Mg _ICP	0.35**	0.32**	K_ICP	0.42*	0.60**
Mn_ICP	-0.24*	-0.22*	Li_ICP	0.17	0.41*
Na_ICP	-0.30**	-0.22*	Mg_ICP	0.31	0.34
Ni_ICP	0.60**	0.60**	Mn_ICP	0.30	0.80**
P_ICP	0.02	0.03	Na_ICP	0.22	0.20
Pb_ICP	-0.15	-0.06	Ni_ICP	-0.09	0.03
S_ICP	0.18	0.05	P_ICP	0.40	0.70**
Sb_ICP	0.50**	0.50**	Pb_ICP	0.30	0.70**
Sr_ICP	0.06	-0.01	S_ICP	0.34	0.65**
V_ICP	-0.51**	-0.40**	Sb_ICP	0.40	0.40
Zn_ICP	0.14	0.22*	Si_ICP	0.12	0.12
Al_XRF	-0.14	-0.03	Sr_ICP	-0.22	-0.50*
Ba_XRF	-0.31**	-0.22*	V_ICP	0.60**	0.75**
Ca_XRF	0.50**	0.26*	Zn_ICP	0.60**	0.80**
Co_XRF	0.16	0.09	Al_XRF	0.60**	0.75**
Cr_XRF	0.40**	0.24*	Ba_XRF	0.62**	0.70**
Cu_XRF	-0.17	-0.31**	Ca_XRF	-0.63**	-0.82**
Fe_XRF	0.40**	0.22*	Co_XRF	0.34	0.60**
K_XRF	0.40**	0.32**	Cr_XRF	-0.06	0.01
Mg_XRF	0.30*	0.14	Cu_XRF	0.46*	0.82**
Mn_XRF	-0.35**	-0.30**	Fe_XRF	0.60**	0.90**
Na_XRF	-0.30**	-0.19	K_XRF	0.60**	.899**
Ni_XRF	0.45**	0.28**	Mg_XRF	0.36	0.38
P_XRF	-0.07	-0.06	Mn_XRF	0.34	0.79**
Pb_XRF	-0.10	-0.12	Na_XRF	0.60**	0.60**
Rb_XRF	0.30**	0.32**	Ni_XRF	0.18	0.41*
S_XRF	0.07	0.03	P_XRF	0.35	0.60**
Si_XRF	-0.51**	-0.32**	Rb_XRF	0.60**	0.94**
Sr_XRF	0.06	-0.02	S_XRF	0.30	0.63**
Ti_XRF	-0.30*	-0.11	Si_XRF	0.62**	0.76**
V_XRF	-0.01	0.04	Sr_XRF	-0.22	-0.46*
Zn_XRF	0.30*	0.16	Ti_XRF	0.61**	0.74**
Zr_XRF	-0.36**	-0.25*	V_XRF	0.42*	0.66**
SIRM	1	0.84**	Zn_XRF	0.51**	0.74**
			Zr_XRF	0.40*	0.60**
			SIRM	1	0.60**

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

8.7.7 Spearman's correlations (R) between the magnetic parameters and element concentrations in the leaf samples from the commercial and the organic vineyards obtained by ICP-OES and WD-XRF

Commercial			Organic		
R	SIRM	χ		SIRM	χ
Al_ICP	-0.05	0.20	Al_ICP	0.06	0.05
As_ICP	0.23*	0.14	As_ICP	0.43	0.00
B_ICP	-0.05	0.30*	B_ICP	0.16	0.15
Ba_ICP	0.30*	0.15	Ba_ICP	0.67**	0.39
Be_ICP	-0.02	-0.05	Be_ICP	-0.17	0.19
Ca_ICP	0.44**	0.04	Bi_ICP	0.70**	0.54*
Cd_ICP	0.03	0.15	Ca_ICP	0.70**	0.42
Co_ICP	0.50**	0.07	Cd_ICP	-0.70**	-0.58*
Cr_ICP	0.60**	0.35**	Co_ICP	0.70**	0.46
Cu_ICP	-0.33**	0.05	Cr_ICP	0.70**	0.38
Fe_ICP	0.13	0.23*	Cu_ICP	-0.39	-0.38
K_ICP	0.19	0.05	Fe_ICP	0.60*	0.28
Mg_ICP	0.30*	-0.02	K_ICP	-0.28	-0.41
Mn_ICP	-0.19	-0.09	Li_ICP	0.60*	0.43
Na_ICP	0.21	0.25*	Mg_ICP	0.60*	0.69**
Ni_ICP	-0.14	-0.10	Mn_ICP	0.40	0.20
Pb_ICP	0.02	0.24*	Mo_ICP	-0.22	-0.16
Sb_ICP	0.30*	0.06	Na_ICP	-0.66**	-0.80**
Sr_ICP	0.50**	0.05	Ni_ICP	-0.03	-0.34
V_ICP	0.07	0.18	P_ICP	-0.27	-0.28
Zn_ICP	-0.20	-0.07	Pb_ICP	-0.65**	-0.67**
Ca_XRF	0.41**	0.02	S_ICP	-0.27	-0.28
K_XRF	-0.30*	0.03	Sb_ICP	-0.38	-0.50
P_XRF	-0.50**	-0.04	Sr_ICP	0.60*	0.36
Mg_XRF	-0.16	0.02	V_ICP	0.15	0.18
Si_XRF	0.33**	-0.02	Zn_ICP	-0.15	-0.20
S_XRF	-0.46**	0.00	Ca_XRF	0.23	-0.12
Al_XRF	-0.18	0.10	K_XRF	-0.60*	-0.55*
Na_XRF	-0.34**	0.11	P_XRF	-0.43	-0.29
Cl_XRF	-0.06	0.14	Mg_XRF	0.43	0.60*
Fe_XRF	-0.30*	-0.03	Si_XRF	0.44	0.26
Mn_XRF	-0.42**	-0.19	S_XRF	-0.73**	-0.56*
Zn_XRF	-0.42**	-0.03	Al_XRF	-0.03	-0.08
Sr_XRF	0.40**	0.03	Na_XRF	-0.53*	-0.26
Cu_XRF	-0.30*	0.03	Fe_XRF	-0.47	-0.33
SIRM	1.00	0.30*	Mn_XRF	0.06	0.08
			Zn_XRF	-0.60*	-0.45
			Cu_XRF	-0.60*	-0.45
			Sr_XRF	0.42	0.23
			SIRM	1.00	0.76**

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Biography

Tijana D. Milićević was born on 23rd January 1989 in Kruševac, the Republic of Serbia, where she finished primary and secondary school. Basic academic studies in Environmental Chemistry at Department of Applied Chemistry, Faculty of Chemistry, University of Belgrade she started in 2008. She graduated in 2012 with a grade 10/10 on Bachelor thesis. Master Academic Studies at the Department of Applied Chemistry, Faculty of Chemistry, University of Belgrade she started 2012, and graduated in 2013 with grade 10/10 on Master thesis entitled *"Поређење различитих типова екстракционих средстава за изоловање елемената који су лакодоступни биљкама"* in Serbian. 2013/2014 she finished Specialisation in the field of Ecological low, Faculty of Law, University of Belgrade. With a grade 8.2/10 (calculated according to Regulation of Doctoral Studies at the University of Belgrade, Gazette of University of Belgrade No. 186/15 and 189/16), 2014 she started PhD studies at Faculty of Chemistry, University of Belgrade. From 2015 to 2017 she was engaged as research trainee and from 2015 until now she has been engaged as a research assistant on the national project *Investigation of climate change and its influences on environment – Monitoring the Influences, Adaptations, and Offsets – III 43007*, Ministry of Education and Science of the Republic of Serbia. She is also engaged on the projects: *European Network for Chemical Elemental Analysis by Total Reflection X-Ray Fluorescence* – COST project and *Neutron activation analysis of environmental samples and new materials* – bilateral cooperation with Joint Institute for Nuclear Research, Dubna, Russia. From 2014, she has been engaged on the project *Plant Tour* organised by "Coca-Cola Hellenic Bottling Company", Serbia. During 2014 she was working as an assistant on two projects: *My city – Green city*, supported by the Secretariat for Environmental Protection, Belgrade and *Biomonitoring of heavy metals in the air along the main roads of the Belgrade city*, supported by the company NIS Novi Sad and the City of Belgrade. In 2017, Tijana got "Erasmus+" grant for student mobility on Department of Bioscience Engineering, University of Antwerp, Belgium, supported by European Commission. She was awarded by SCOPES Grant for attending the 14th International Conference on the Biogeochemistry of Trace Elements ICOBTE sponsored by a specific program of the Swiss National Science Foundation for conference grants. Tijana is a coauthor of five scientific papers published in the

international journals, form which four resulted from this doctoral dissertation and the fifth is also from the field of environmental science. She is an author of one chapter in the book (publisher Springer), one chapter in monograph (publisher Mission OECS − the Organization for Security and Co-operation in Europe, in Serbia), 6 extended abstracts and 14 abstracts published in books of abstracts on international and national conferences.

Биографија

Тијана Д. Милићевић рођена је 23. јануара 1989. године у Крушевцу, Република Србија, где је завршила основну школу и Гимназију. Основне академске студије на Катедри за примењену хемију Хемијског факултета Универзитета у Београду (смер: хемија животне средине) уписала је школске 2008/09. године. Дипломирала је 2012. године са оценом 10 на завршном раду. Мастер академске студије на Катедри за примењену хемију Хемијског факултета Универзитета у Београду (смер: мастер хемичар) уписала је школске 2012/13. године. Мастер рад под називом „Поређење различитих типова екстракционих средстава за изоловање елемената који су лакодоступни биљкама“ одбранила је 2013. године са оценом 10. Током школске 2013/14. уписала је Студије за иновацију (специјализацију) знања из области Еколошко право на Правном Факултету Универзитета у Београду и успешно је одбранила завршни испит. Са општом просечном оценом 8,2 (израчунатом према Правилнику о докторским студијама на Универзитету у Београду, *Гласник Универзитета у Београду број 186/15 и 189/16*) са претходних нивоа студија, школске 2014/15. године уписала је докторске академске студије на Катедри за примењену хемију Хемијског факултета у Београду (студијски програм: Хемија). Била је ангажевана од 2015. до 2017. као истраживач приправник, а од 2017. је ангажована као истраживач сарадник на пројекту „Истраживање климатских промена и њихов утицај на животну средину – праћење утицаја, адаптација и ублажавање” (бр. ИИИ43007) финансираног од стране Министарства просвете, науке и технолошког развоја Републике Србије. Тијана је ангажована на пројектима: „*European Network for Chemical Elemental Analysis by Total Reflection X-Ray Fluorescence“, COST* пројекат и „Neutron activation analysis of environmental samples and new materials“, билатерална сарадња са Обједињеним институтом за нуклеарна истраживања (JINR), Дубна, Русија. Од 2014. године ангажована је као сарадник на пројекту *„Plant Tour“* у *„Coca Cola Hellenic Botteling“* компанији. Током 2014. године је учествовала у реализацији два пројекта: едукативног пројекта „Мој град – Зеленград“ у организацији фондације „Ecotopia“ који је подржан од стране Секретеријата за заштиту животне средине Града Београда и истраживачког

пројекта „Биомониторинг тешких метала у ваздуху дуж главних саобраћајница града Београда“ подржаном од компаније НИС а.д. и Града Београда.

Добитник је стипендије Европске Комисије за усавршавање у иностранству (Еразмус+), на Катедри за биоинжењерство Природно-математичког факултета Универзитета у Антверпу, Белгија (Departement of Bioscience Engineering, Faculty of Sciences, University of Antwerp, Antwerp, Belgium) где је боравила од јануара до априла 2017. Такође, добитник је гранта Швајцарске националне фондације за развој науке у оквиру програма подршке учешћа младих истраживача на међународном скупу „The International Conference on the Biogeochemistry of Trace Elements ICOBTE“, 16−21. јула 2017. године, у Цириху, Швајцарска. Тијана је коаутор пет научних радова публикованих у међународним часописима, од којих је четири, на којима је први аутор, проистекло из ове дисертације (један је публикован у међународном часопису изузетних вредности M21a, а три су публикована у врхунским међународним часописима M21), а један рад на коме је коаутор је такође из области животне средине (публикован у међународном часопису изузетних вредности M21a), Аутор је једног поглавља у књизи (издавач „*Springer“*) и једног поглавља у монографији (издавач Мисија ОЕБС у Србији), аутор је 6 саопштења штампаних у целини и 14 саопштења штампаних у изводу на интернационалним и националним скуповима.

Прилог 1.

Изјава о ауторству

Име и презиме аутора Тијана (Драгомир) Милићевић

Број индекса ДХ01/2014

Изјављујем

да је докторска дисертација под насловом:

An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil−plant−air system: bioavailability and biomonitoring

(Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг)

- резултат сопственог истраживачког рада;
- да дисертација у целини ни у деловима није била предложена за стицање друге дипломе према студијским програмима других високошколских установа;
- да су резултати коректно наведени и
- да нисам кршио/ла ауторска права и користио/ла интелектуалну својину других лица.

Потпис докторанда

У Београду, 28.09.2018. године

_____

Пилог 2.

Изјава о истоветности штампане и електронске верзије докторског рада

Име и презиме аутора Тијана Милићевић

Број индекса ДХ01/2014

Студијски програм Доктор хемијских наука

Наслов рада An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil−plant−air system: bioavailability and biomonitoring (Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг)

Ментор др Александар Поповић, редовни професор Хемијског факултета, Универзитета у Београду и др Мира Аничић Урошевић, виши научни сарадник Института за физику Београд, Универзитета у Београду

Потписани Тијана Милићевић

Изјављујем да је штампана верзија мог докторског рада истоветна електронској верзији коју сам предао/ла ради похрањена у **Дигиталном репозиторијуму Универзитета у Београду.**

Дозвољавам да се објаве моји лични подаци везани за добијање академског назива доктора наука, као што су име и презиме, година и место рођења и датум одбране рада.

Ови лични подаци могу се објавити на мрежним страницама дигиталне библиотеке, у електронском каталогу и у публикацијама Универзитета у Београду.

Потпис докторанда

У Београду, 28.09.2018. године

_____

Прилог 3.

Изјава о коришћењу

Овлашћујем Универзитетску библиотеку „Светозар Марковић“ да у Дигитални репозиторијум Универзитета у Београду унесе моју докторску дисертацију под насловом:

An integrated approach to the investigation of potentially toxic elements and magnetic particles in the soil−plant−air system: bioavailability and biomonitoring

(Интегрисани приступ истраживању потенцијално токсичних елемената и магнетних честица у систему земљиште–биљка–ваздух: биодоступност и биомониторинг)

која је моје ауторско дело.

Дисертацију са свим прилозима предао/ла сам у електронском формату погодном за трајно архивирање.

Моју докторску дисертацију похрањену у Дигиталном репозиторијуму Универзитета у Београду и доступну у отвореном приступу могу да користе сви који поштују одредбе садржане у одабраном типу лиценце Креативне заједнице (*Creative Commons*) за коју сам се одлучио/ла.

1. Ауторство

2. Ауторство – некомерцијално

3. Ауторство – некомерцијално – без прерада

4. Ауторство – некомерцијално – делити под истим условима

5. Ауторство – без прерада

6. Ауторство – делити под истим условима

(Молимо да заокружите само једну од шест понуђених лиценци.
Кратак опис лиценци је саставни део ове изјаве).

Потпис докторанда

У Београду, 28.09.2018. године

_____

1. Ауторство. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце, чак и у комерцијалне сврхе. Ово је најслободнија од свих лиценци.

2. Ауторство – некомерцијално. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца не дозвољава комерцијалну употребу дела.

3. Ауторство – некомерцијално – без прерада. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца не дозвољава комерцијалну употребу дела. У односу на све остале лиценце, овом лиценцом се ограничава највећи обим права коришћења дела.

4. Ауторство – некомерцијално – делити под истим условима. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца не дозвољава комерцијалну употребу дела и прерада.

5. Ауторство – без прерада. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца дозвољава комерцијалну употребу дела.

6. Ауторство – делити под истим условима. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца дозвољава комерцијалну употребу дела и прерада. Слична је софтверским лиценцама, односно лиценцама отвореног кода.