

DISTRIBUTION OF ZINC IN VINEYARD AREAS TREATED WITH ZINC CONTAINING PHYTOPHARMACEUTICALS

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Abstract

Zinc concentration in vineyard soil is, in general, increased markedly by the long term application of zinc containing fungicides. The most significant source of Zn are nowadays dithiocarbamate based fungicides, e.g. Antracol. The concentration of total zinc and EDTA- and ammonium lactate (AL) extractable Zn in soils are evaluated together with the concentration of Zn in different inorganic fertilizers and in fungicides. The results of the study indicate that in the observed vineyard areas a long term accumulation of zinc appears. The study was made in vineyards of Kalvarija and Meranovo (Maribor, Slovenia).

1. Introduction

Contamination of vineyard soils with zinc results from the use of phytopharmaceutical substances containing zinc and from the use of mineral fertilizers. Fungicide Antracol containing 70 % of zinc-propylene-bis-dithiocarbamate (active compound Propineb) has been largely used for vineyard protection. Active compound Propineb contains Zn (22,6 %, calculated from molecular weight). Phytopharmaceutical fertilizer Antracol contains 16 % of Zn, Mancozeb 2,5 % of Zn, Bercema-Zineb 17 % of Zn and Supertol 12 % of Zn.¹

1000 to 1500 kg/ha of various mineral fertilizers is consumed annually in intensive production. In mineral fertilizers we can find in average up to 500 mg of Zn/kg (ammonium sulphate, superphosphate, limestone, complex fertilizers) and in raw phosphates up to 1000 mg Zn/kg.²

Mobility of zinc in soil is closely connected to soil reaction. With increased acidity of soil there is also an increase in the quantity of element available to plants. Content of

zinc is considerably lower in acid than in alkaline soil. Zinc is hard to wash away therefore the contents of zinc are the highest in the surface layer.^{3,4}

Contents of zinc in Slovene soil in the country area was researched by Andjelov, M. and Šajn, R.^{5, 6} Increased contents of zinc were established in the Carinthia area (the Mežica mine), in Celje area (the Celje zinc factory) and in the areas of intensive plantation production of fruit and grape (organometallic phytopharmaceutical pesticides and fertilizers).

The mass of root system using mineral nutrients from soil is at depth of 20 to 50 cm. With fruit and grape production 100 to 200 g of zinc per ha (10^4 m²) are consumed annually. With the use of carbamate fungicides we annually add 3 to 5 kg of zinc per one ha of vineyard surface. The addition being significantly larger than the uptake the deficiency of zinc in soil does not occur with intensive technology unless phosphate ion is involved in the metabolism.⁷

Vineyard soil contains 3 to 8 mg kg⁻¹ EDTA-extractable zinc.² Zinc concentration in soil increases annually from 0,5 to 1 mg kg⁻¹ due to the use of fungicides and fertilizers containing zinc.

Growth, development and consequently production are limited by the nutrient existing in relatively the lowest quantity. Considerable deficiency as well as larger surplus of specific nutrients can be detected on vine by visual inspection. Zinc deficiency of vine occurs in the situation where in soil rich with phosphorus phosphate ions surround the roots causing the change of zinc ions to insoluble zinc phosphate when contacting the roots. The surplus of phosphate ions deactivates zinc ions into insoluble zinc phosphate as well.

From the viewpoint of the chemistry of soil the most important property of clay minerals is adsorption and cation exchange. In alkaline soil the dominant reaction is the exchange of Zn²⁺ with Ca²⁺ followed by Zinc precipitation as a consequence of decreased solubility of the component. Inorganic ligands (OH⁻, CO₃²⁻, HPO₄²⁻ and PO₄³⁻) in alkaline soil successfully compete with chelating ligands at formation of

insoluble components.⁸ Exchanging cations represent plant available reserve of those plant nutrients which are available in the form of cations. Availability of each cation depends on the relationship between entire cation exchange capacity of a certain ion (saturation percentage) and relative quantity of the remaining cations. Exchange of cations on clay in soil is also influenced by the type, valence and concentration of a cation. It is important for permanent soil fertility to keep the quantity and mutual proportion of exchanging cations in such range and balance that is appropriate for growth and demands of plants. When adding different salts as fertilisers to soils, part of cations adsorb on adsorption complex and equivalent quantity of another cation releases from the complex becoming available to plants.

The purpose of our work is to research the influence of organometallic phytopharmaceutical fertilizers use on zinc dynamic and distribution. We used control soil samples in our research for differentiating natural contents of chemical elements from situation caused by human activities. Content of elements in a control sample gives natural soil profile including the atmospheric influence. We determined complete contents of zinc and EDTA- and AL- (ammonium lactate) extractable (plant available) zinc with flame atomic absorption spectrometry (FAAS) technique. Content of zinc was determined in wine samples from vineyards included in research. We calculated weight balance from the data on zinc content in wine (zinc uptake) and content of zinc in used phytopharmaceutical substances (zinc addition). We measured zinc content in the sediment of stream at a foothill of the vineyard. We sampled the sediment on several sites from the spring to the mouth of the river Drava. We wished to prove increased zinc concentration in the stream sediment as a consequence of the use of phytopharmaceutical substances containing zinc.

2. Experimental

Zinc and copper were determined by flame atomic absorption spectrometer, SpectrAA-10 (Varian, Mulgrave, Australia) in air/acetylene flame. Zinc absorption was measured with the use of deuterium lamp for background correction at 213,9 nm wavelength and copper absorption at 324,7 nm wavelength.

Potassium concentration was determined by flame atomic absorption spectrometer, SpectrAA-10 (Varian, Mulgrave, Australia) measuring potassium emission in air/acetylene flame at 766,5 nm wavelength.

Phosphorus concentration was determined by spectrophotometric ammonium molybdate method⁹ (MAS) on Varian Cary 1E spectrophotometer (Varian, Mulgrave, Australia) at 659 nm wavelength.

Soil samples were digested in PFTE (polytetrafluoroethylene) containers in MDS 2000 microwave oven produced by CEM (CEM; Matthews n.c., USA)

For measuring pH in solution Iskra MA 5750 pH meter was used (Iskra, Horjul, Slovenia) with HEC 0101 combined glass electrode.

3. Procedure

Chemical elements in soil available to plants are determined from soil extracts by AL- and EDTA- extraction solution.

AL-extraction solution: solution of hydrated lactic acid was prepared by adding 500 cm³ of distilled water to 250 g of lactic acid and heating the solution for 48 hours in sterilizer at temperature of 368 K. The amount of water which evaporated during the heating process was replaced as necessary. After cooling the solution we determined its multiple concentration by adding 50 cm³ of distilled water and 3 drops of phenolphthalein to 1 cm³ of hydrated lactic acid solution and titrated it with 0,1 mol dm⁻³ concentration of sodium hydroxide solution.

Concentration of hydrated lactic acid solution was approx. 3 mol dm⁻³ (c₁). Ammonium lactate solution (AL) was prepared by adding 187,5 g (178,5 cm³) of 96 % acetic acid and 77,0 g of ammonium acetate to 1000/c₁ g of hydrated lactic acid in 1000 cm³ volumetric flask and adding distilled water to the mark. What we got was a basic AL-solution of which pH should equal 3,8. If it comes to any discrepancies we should balance pH of solution by adding ammonium hydroxide solution or acetic acid. AL-extraction solution was prepared by 10 times diluting the basic AL-solution.

EDTA extraction solution: 18,612 g of EDTA (disodium salt of ethylenediamine-tetraacetic acid dihydrate $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) was dissolved in distilled water and made up to 1000 cm^3 volume. Concentration of thus prepared EDTA was $0,05\text{ mol dm}^{-3}$.

Sampling

We sampled soils of two vineyard from both riverbanks of the river Drava near Maribor. Surface of the Orlica vineyard in Meranovo is 50000 m^2 with 17800 vines. Surface of the Kalvarija vineyard is 45000 m^2 with 15000 vines. We chose the particular vineyards for their diversity in acidity of soil. Orlica possesses acid soil whereas Kalvarija possesses alkaline soil. We sampled control soil sample above the two vineyards on uncultivated surfaces. The distance between sampling sites was approx. 10 m. We took the samples with metal probe with 2 cm in diameter at depth of 0-20 cm. We sampled according to ÖNORM L1057 which regulates soil samples taking in vineyards and orchards.¹⁰

We dried the soil samples in the air to their constant weight. We removed larger stones and roots from dried samples, ground them in the mill and passed them through 1-mm sieve. Humidity was determined by weighing 10 g of air-dried sample into paper bag and drying it in a drying machine at 333 K to the constant weight. We calculated the results of heavy metals content according to the dry weight of the sample.

Analysis procedures

Microwave-assisted digestion of soil samples with aqua regia¹¹: we weighed $0,5000 \pm 0,0001\text{ g}$ of air-dried soil sample in PTFE container, added 16 cm^3 of aqua regia (HNO_3 and HCl , 1+3). We covered the containers and put them in the microwave oven. Heating programme for 12 container was the following: 1 minute at 180 W, 4 minutes at 480 W and finally 60 minutes at 650 W. We cooled the containers to room temperature. We poured the contents through wrinkled filter paper (MN 619^{1/4}) into 50 cm^3 volumetric flask and added deionized water to the mark. Copper and zinc concentration in filtrate were determined by the FAAS method in air/acetylene flame. Calibration curve was

prepared with standard solutions added the same amount of aqua regia as the samples. We prepared a blank sample for controlling acid purity.

Total microwave-assisted digestion of soil samples: in PTFE container for digestion we weighed $1,0000 \pm 0,0001$ g of air-dried soil sample and added 10 cm^3 of deionized water, 5 cm^3 of HNO_3 , 2 cm^3 of HCl and 3 cm^3 of HF . We covered the containers and put them in the microwave oven.

We programmed the pressure control on $6,9 \cdot 10^5$ Pa. We heated twelve containers for 60 minutes at 650 W. As the pressure in the containers reached the control pressure we continued to heat the containers for another 30 minutes. We cooled the containers to room temperature and poured the content through wrinkled filter paper into 50 cm^3 PE volumetric flask as well as added deionized water to the mark. Copper and zinc concentration in the filtrate were determined by FAAS method in air/acetylene flame. Calibration curve was prepared with standard solutions added the same amount of acids as the samples. We prepared a blank sample for controlling acid purity.

Extraction of soil samples in EDTA-solution: $10,000 \pm 0,001$ g of fine air-dried soil sample were weighed to 250 cm^3 plastic container and poured over by 100 cm^3 concentration of EDTA-solution ($0,05 \text{ mol dm}^{-3}$). The plastic container was sealed and shaken on horizontal shaker for two hours with 180 turns per minute. After the shaking process the suspension was filtered through wrinkled filter paper. We discarded first few ml of the filtrate. Concentration of copper, zinc, iron and manganese in the filtrate was determined by the FAAS method.

Soil sample extraction with AL – solution: into plastic container with cover we weighed $5,000 \pm 0,001$ g of soil sample and added 100 mL of AL-extraction solution. We covered the container and shook it for two hours on rotary shaker at 35 turns per minute. Suspension was filtered through dry wrinkled filter paper of medium porosity (white strip). First few ml of the filtrate were discarded. We determined phosphorus concentration in the filtrate by measuring molecular absorption at 659 nm wavelength and potassium concentration by measuring potassium atoms emission at 766,5 nm wavelength in air/acetylene flame,⁹ AL-extraction solution served as a blank sample.

Soil acidity was determined according to ÖNORM¹², free carbonates by Scheibler¹³.

4. Results and discussion

Linear range, detection limit and quantitation limit for zinc, phosphorus and potassium determination methods are shown in Table 1. Precision of total zinc determination method in soil samples is shown in Table 2. According to both Tables the sensitivity, regularity and precision of analytical values are satisfactory.

Table 1: Linear ranges, detection and quantitation limits for the determination of Zn by FAAS, P by MAS and K by FAES

	Linear range (mg L ⁻¹)	Detection limit (mg L ⁻¹)	Quantitation limit (mg kg ⁻¹)
Zn - aqua regia	0,2 - 7,0	0,003 - 0,013	0,84 - 2,66
Zn - EDTA	0,2 - 1,0	0,005	0,05
Zn - AL	0,2 - 1,0	0,001	0,02
P ₂ O ₅	0,1 - 4,0	0,0002	0,03
K	1,0 - 4,0	0,066	13,2

Table 2: Precision of total Zn content determination in SRM 2709

Element	^a X (mg kg ⁻¹)	^b RSD (%)	^c TIM
Zn	105	1,5	3,5

^aMean concentration, result of ten determinations of the same sample.

^bRelative standard deviation.

^cTrust interval of measurements at 95 % reliability

To verify the accuracy of total determination of zinc concentration we simultaneously analysed standard reference material 2709 (San Joaquin Soil, National Institute of Standards and Technology). Comparison of our results with certified values in reference material is given in Table 3. Table 3 shows the total measured value of zinc to be well matched with certified values for standard reference material.

Table 3: Comparison of Zn results with certified values for SRM 2709

Element	Certified values (mg kg ⁻¹)	Measured values (mg kg ⁻¹)
Zn	106 ± 3	105 ± 3

In Table 4 pH values (potential and active soil acidity) and free carbonates content in soil of sampled vineyards and control samples are shown.

Table 4: Free carbonate content and soil samples pH value

Soil sample	Free carbonates (%)	Potential acidity pH	Active acidity pH
Orlica control	0,8	4,0	4,8
Orlica	2,2	5,8	6,2
Kalvarija control	3,0	6,3	7,0
Kalvarija 2	18,8	7,4	7,7
Kalvarija 3	11,1	7,6	7,6

Control soil sample was taken on uncultivated surfaces above the vineyard where there has never been any fertilizing or spraying with pesticides. We presumed that the elements content in control sample provided natural soil profile including atmospheric influence.

Free carbonates content is significantly lower in control soil samples than in vineyard soil samples. The same goes for pH values which are again lower in control samples. In both cases this is the consequence of calcifying acid soil in vineyards. Acid soil is neutralised with the use of lime which increases pH soil value and quantity of calcium and magnesium available to plants and at the same time decreases quantity of free iron, aluminium and manganese. For liming vineyard soil calcium carbonate (CaCO_3) is used.

Measured values of potential acidity are somewhat lower in comparison to active soil acidity. The exception is the Kalvarija 3 soil sample where potential and active acidity have the same value and there is no need for bound protons.

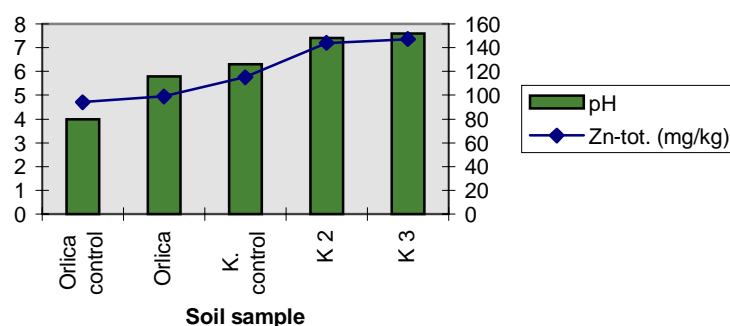
In order to study the level of acid extraction we made comparative analyses of soil samples digested in the microwave oven with various acid mixtures. Total microwave-assisted digestion (HNO_3 , HCl , HF) of soil sample for Zn analysis was compared with microwave digestion with aqua regia (HNO_3 , HCl). Results of comparative analysis are shown in Table 5.

Table 5: Zinc content in soil samples after microwave assisted digestion in aqua regia and after total acid digestion in microwave oven determined by FAAS, n=5

Soil sample	Aqua regia microwave ass. digestion Zn (mg kg ⁻¹)	Total microwave ass. digestion Zn (mg kg ⁻¹)
Orlica control	94	94
Orlica	99	100
Kalvarija control	115	115
Kalvarija 2	144	147
Kalvarija 3	147	149
SRM 2709	105	107

Zinc contents in SRM 2709 after aqua regia microwave-assisted digestion and after total acid digestion in the microwave oven are in the random mistake range. Table 5 shows somewhat lower values of zinc in soil samples after aqua regia microwave-assisted digestion in comparison to zinc values in the same samples digested in acid mixture HNO₃, HCl and HF. Aqua regia digestion of soil samples in the microwave oven does not give the same results we get with total digestion of soil sample in the microwave oven, yet zinc contents measured after both digestions remain in the range of measurement instability and are compatible with certified values. Consequently we presume that zinc content can be measured in soil samples digested with aqua regia without adding hydrofluoric acid.

Acid soil reaction is caused by the lack of exchanging metal ions. Zinc content is therefore much lower in acid that in alkaline soil. We compared total zinc content in vineyard soil samples and control samples to pH value of the samples. Comparison results are shown in Figure 1.

**Figure 1:** Correlation between total zinc content and pH soil value

Correlation between pH soil values and zinc content is clearly evident from Figure 1. Total zinc content in analysed vineyard soil samples and control samples increases together with pH soil value.

We used EDTA- and AL- extraction solution for determination of zinc available to plants. Table 6 shows the fraction of total plant available zinc in soil.

Table 6: Fraction of plant available zinc in soil samples

Soil samle	Zn EDTA (mg kg ⁻¹)	Zn total (mg kg ⁻¹)	Extractable/Total ratio (%)
Orlica control	7	94	7,4
Orlica	8	99	8,1
Kalvarija control	4	115	3,5
Kalvarija 2	13	144	9,0
Kalvarija 3	17	147	11,6

Only 3 to 12 % of total zinc content in analysed soil samples are actually taken up by plants.

Figure 2 shows total, AL- and EDTA- extractable concentrations of Zn in soil samples.

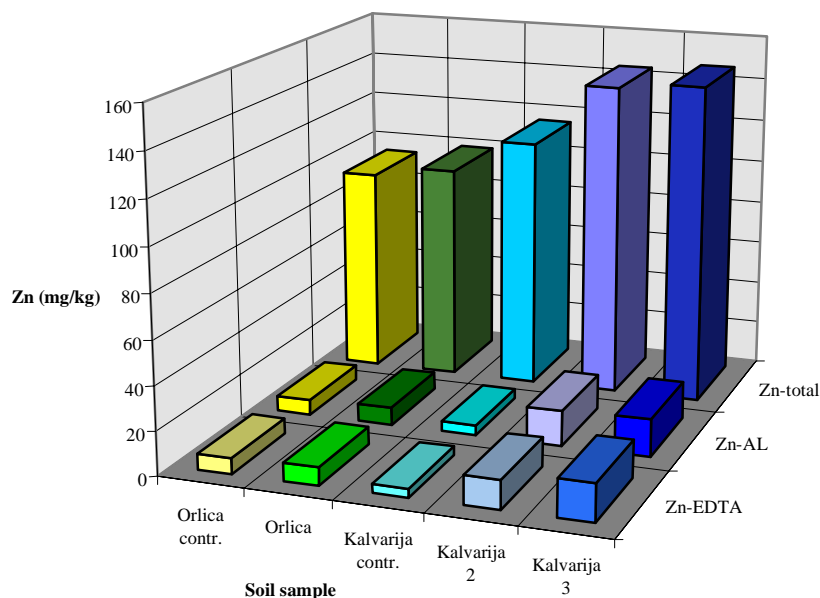


Figure 2: Content of total, AL- and EDTA-extractable zinc in soil samples.

Nature soil contains enough of zinc for vine uptake. Zinc fungicides further increase zinc content. In low acid to alkaline soil zinc deficiency can be caused by high phosphorus concentration due to formation of phosphates hard to dissolve.

P and K content in soil samples and control samples is shown in Table 7.

Table 7: Determination of phosphorus content with MAS and potassium content with FAES in samples of AL- soil extracts, n=5

Soil sample	Phosphorus as P ₂ O ₅ (mg / 100 g)	Potassium as K ₂ O (mg / 100 g)
Orlica control	2,1	25,9
Orlica	18,6	43,7
Kalvarija control	2,7	34,1
Kalvarija 2	50,0	80,2
Kalvarija 3	52,9	76,2

Phosphorus and potassium content in control soil samples (uncultivated surfaces) is lower than the content of both elements in vineyard soil. Considerable difference is noted in the case of phosphorus concentration of which is ten times higher in vineyards than in control samples.

Proportion between Al-extractable phosphorus and zinc content in vineyard soil samples and control soil samples is shown in Table 8 and graphically in Figure 3.

Table 8: Phosphorus and zinc content in Al-extracts of soil samples. P/Zn proportion.

Soil sample	P (AL-soluble) (mg kg ⁻¹)	Zn (AL-soluble) (mg kg ⁻¹)	P/Zn proportion
Orlica control	4,6	7	0,7
Orlica	40,6	8	5,1
Kalvarija control	5,9	4,5	1,3
Kalvarija 2	109,1	16	6,8
Kalvarija 3	115,4	17	6,8

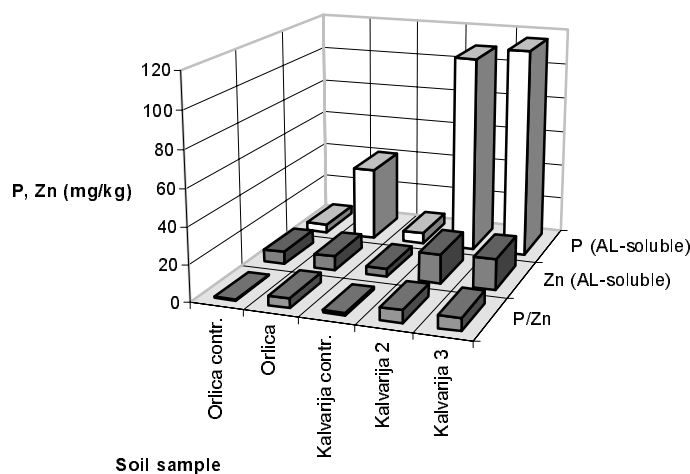


Figure 3: Content of Al-soluble zinc and phosphorus in soil samples. P/Zn proportion.

Phosphorus and zinc proportion is much higher in intensively cultivated soil samples (5 to 7 times) than in control soil samples. High phosphorus content in vineyard soil samples is caused by mineral fertilization containing phosphorus (superphosphate, Thomas phosphate, complex NPK fertilizers, ...).

8 kg of Cu-Antracol fungicide, 5 kg of Dithane M-45 fungicide and 2,5 kg of Antracol Combi fungicide per ha is annually consumed for the protection of the Orlica vineyard. Phytopharmaceutical agent Antracol contains 70 % of active compound Propineb, Cu-Antracol 45,6 % and Antracol Combi 25 %. Active compound propineb contains 22,6 % of zinc (calculated from molecular weight). Phytopharmaceutical substance Antracol therefore contains 15,8 % of zinc, Cu-Antracol 10,3 % Zn and Antracol Combi 5,6 %. After Dithane M-45 aqua regia microwave digestion we determined by FAAS 2,1 % of Zn in fungicide. We measured the content of total and water soluble zinc in phytopharmaceutical substance Antracol. Antracol contains 12,5 % of total and 0,2 % of water soluble zinc.

Addition and uptake of zinc in the Orlica vineyard was calculated. Annual zinc addition in the Orlica vineyard was calculated from zinc content data in phytopharmaceutical substances used for vineyard protection in one-year period. Data is shown in Table 9.

Table 9: Zinc content in pesticides used for Orlica vineyard protection in year 1996.

Pesticides	Dosage (kg)	Zn (%)	Zn (g)
Cu - Antracol	40	10,3	4120
Antracol Combi	12,5	5,6	700
Dithane M-45	25	2,1	525

Annual zinc addition with fertilizers and pesticides amounts to 5345 g or 5,3 kg per vineyard surface which is 1,1 kg of zinc per ha. Annual use of various mineral fertilizers in intensive production being 1000 to 1500 kg/ha the quantity of zinc in these fertilizers should also be taken into account. Since 1996 the vineyard Orlica is not treated with mineral fertilizers. Zinc concentration increases annually for 0,4 mg per 1 kg of soil due to the use of zinc containing phytopharmaceutical substances and mineral fertilizers.

Zinc uptake was calculated from zinc content data in Sauvignon Meranovo 1997 and amount of wine produced in the Orlica vineyard. We determined zinc content in wine by standard addition method on flame AAS apparatus. Wine contained 0,52 mg Zn dm⁻³. Estimated quantity of wine produced in the Orlica vineyard (the Meranovo area) is 24000 dm³ meaning that our zinc uptake from Orlica is 12,5 g per year with wine. Total amount of zinc was not included in wine analysis. We did not determine the part of zinc in lees and the rest of the vine (leaves, shoots, ...). Our annual zinc uptake with grapes is approx. 100 g/ha.⁷ We also have to consider transfer of zinc caused by rain to the nearest waters. To establish whether intensive vineyard cultivation influences the level of zinc in surface waters we analysed the sediment of the Meranovo stream which springs in the Pohorje territory above the vineyard, and runs below the vineyard to the river Drava. Zinc content in the sediment is shown in Table 10.

Table 10: Zinc content in the Meranovo stream sediment

Sampling site	Date	Zn (mg kg ⁻¹)
Spring	25.5.'96	96
Below the vineyard	25.5.'96	95
Behind the vineyard	25.5.'96	120,5
Mouth of the Drava	25.5.'96	130

Zinc content in the stream sediment is approximately the same from the spring the vineyard area and somewhat higher after the stream leaves the vineyard. The highest zinc content was determined in the sediment taken from the mouth of the Drava river. Rain washes away vineyard soil and the silt gathers in streams. Zinc concentration in the stream sediment being much lower before the stream reaches the vineyard than after it leaves it we can deduce that the increased zinc content is a consequence of spraying the vineyard with zinc containing phytopharmaceutical substances. The addition of zinc is larger than the uptake in the Orlica vineyard therefore zinc must accumulate in soils.

5. Conclusions

Free carbonates content is in control soil samples considerably lower than in vineyard soil samples. pH value as well is lower in control samples than pH in vineyard soil samples. Both is the consequence of calcifying process in vineyards acid soil.

Total zinc content increases together with pH soil value in analysed vineyard soil samples and control samples. From total zinc quantity in analysed samples only 3 to 12 % are consumed by plants.

Proportion between AL- extractable P and Zn content is 5 to 7 times higher in intensively cultivated soil samples than in control samples. High P content in vineyard soil samples is caused by phosphorus containing mineral fertilizers (superphosphate, Thomas phosphate, complex NPK fertilizers, ...). High Zn content in vineyard soil is caused by use of zinc containing organometallic phytopharmaceutical substances.

Long term use of mineral fertilizers in wine growing is the cause for significantly higher P and K content in vineyard soil samples than in control soil samples.

Zinc addition in the Orlica vineyard soil in Meranovo is much larger than uptake, the consequence being accumulation of zinc in soil. Analysis of the Meranovo stream sediment which springs in the Pohorje territory and runs below the vineyard to river Drava showed much lower zinc concentration in the stream sediment before the stream reaches the vineyard than after it leaves the vineyard. From this we infer that the increasing zinc content in the sediment is caused by the use of zinc containing phytopharmaceutical substances and mineral fertilizers.

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Povzetek

Cink je sestavni del aktivne komponente Antracol-a, ki se v vinogradništvu veliko uporablja kot kontaktni fungicid. Zato predstavlja uporaba tovrstnih fungicidov potencialno nevarnost za kontaminacijo vinogradniških tal s cinkom. Ugotovili smo, da je povečana koncentracija cinka v vinogradniških tleh v glavnem posledica dolgoletne uporabe organokovinskih fitofarmaceutskih pripravkov. Diskutirane so koncentracije celokupnega in rastlinam dostopnega cinka v tleh, kakor tudi koncentracije Zn v organokovinskih fitofarmaceutskih pripravkih. Raziskava je potekala na vinogradniških področjih Kalvarija in Meranovo (Maribor, Slovenija).