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CONTENT OF HEAVY METALS AND SULPHUR IN FRUITS SAMPLED IN VICINITY OF MINING-METALLURGICAL COMPLEX

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ABSTRACT
The pollution emitted into the air from mining-metallurgical complex negatively affects the environment. Plants have the ability to accumulate pollutants in their tissues. The concentration of heavy metals Ni, Zn, Mn and Cu, as well as sulphur, were determined in the edible parts of fruits. The fruits of apple, pear, peach and apricot trees were sampled in rural areas in the vicinity of the industrial complex. Cluster analysis showed grouping of Ni, Mn and Zn into one cluster, while Cu and S were grouped into the other clusters due to high concentrations in fruit samples. High concentrations of Cu and S indicate contamination of the fruits. These elements could also originate from the mining-metallurgical complex or from excessive use of chemicals for plant protection against diseases and pests.
Keywords: Fruits, Air pollution, Heavy metals, Sulphur, Mining-metallurgical complex

1. INTRODUCTION
Native plants are good indicators of ambient air quality and its growth media. Plants absorb airborne anthropogenic pollutants, and their chemical composition may be a good indicator for contaminated areas when it is assessed against background values obtained for unpolluted vegetation. The bioavailability of trace elements from aerial sources through the leaves may have a significant impact on plant contamination. Another significant source of contamination is foliar applications of fertilizers, especially of elements such as Fe, Mn, Zn, and Cu.
Optimum quantity of Mn, Zn, Ni, Cu and other elements is the main precondition for the proper growth and development of plants. However, high concentrations of these elements can have a negative and toxic effect on plants [1]. Sulphur is one of the essential elements for many functions in plants, such as synthesis of chlorophyll. However, sulphur deficiency could reduce plant growth, quality and resistance to pests and diseases [2].
Seasonal fruits and vegetables represent a source of nutrients and can contain toxic elements as well, which can cause the appearance of some chronic diseases in humans [3,4]. Emission from anthropogenic pollution sources increases the concentration of pollutants in the environment, which poses a potential threat to fruit and vegetables grown in polluted areas [4]. Saracoglu et al. (2009) considered that determination of toxic elements in fruits consumed in large quantities is necessary [3]. Unlike vegetables, the accumulation of heavy metals in fruits is low because a large proportion of heavy metals absorbed by trees is stored in other organs, especially in leaves [4]. Başar (2006) confirmed that concentrations of Mn, Zn, Cu and Ni are higher in leaves than in peach fruit [5].

Concentrations of elements are often determined in fruits (apricot, apple, pear, peach, plum), which are also grown in the studied area [3-6].
The aim of this paper was to determine heavy metal and sulphur content in fruits grown in rural areas in the vicinity of mining and metallurgy complex in Bor.

2. DESCRIPTION OF THE STUDY AREA

The municipality of Bor is located in the central part of Eastern Serbia on the Balkan Peninsula. The basic activities in the study area are mining and metallurgical processing of copper ores, which started back in 1902. The present copper smelter was built during the 1961–1968 period and it is the biggest source of SO_2 and particulate matter emissions in Serbia [7]. Sulphide copper concentrate, which is melted in the smelter, contains accompanying elements As, Pb, Zn, Hg, Cd, Fe, Mn, as well as precious metals Ag, Au, etc. [8].
Air pollution originating from mining and metallurgy complex, as well as dust from ore waste and flotation tailing ponds are transported to the surrounding rural settlements. In Figure 1, a map of Bor is shown with the sampling sites of fruits from nine rural settlements (Oštrelj, Slatina, Brestovac, D.B. Reka, Brestovac spa, Brezonik, Gornjane, Metovnica, Zlot).

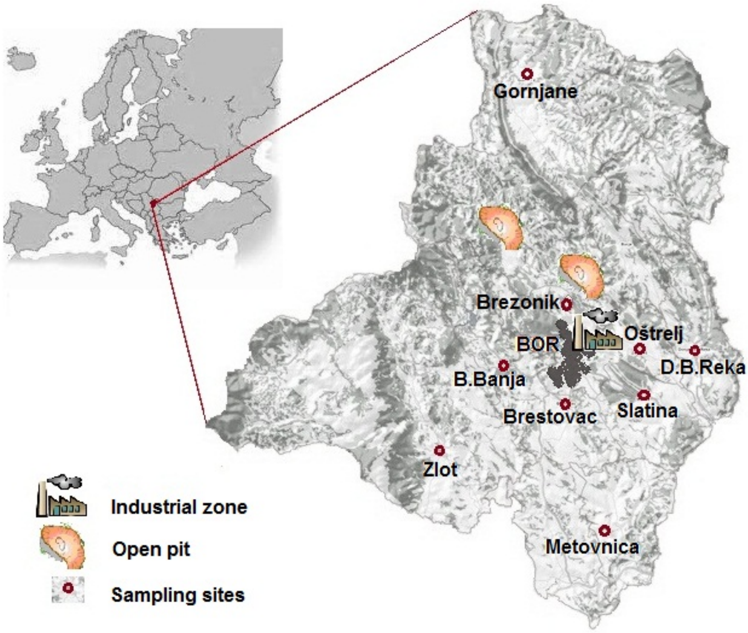

Figure 1. Map of Bor and its surroundings showing sampling sites

3. EXPERIMENTAL

The fruits of apple, pear, peach and apricot are sampled for the analysis of heavy metals and sulphur in fruits. Samples were collected from June to early September. The fresh samples were washed using distilled water in order to remove dust particles, then chopped with stainless steel blade and oven-dried at 50°C until constant weight. The dried samples were ground in a laboratory mill into fine powder. Prepared samples of fruits were digested according to the Method 3050B [9]. Content of heavy metals (Cu, Mn, Zn, Ni) and S in samples was analyzed using ICP-AES. The concentrations of all the determined elements are expressed as mg kg^{-1} of dry weight.

4. RESULTS AND DISCUSSION

The content of Mn, Ni, Zn, Cu and S in the fruits (apple, pear, apricot and peach) is given in Table 1. Based on the mean concentration of the elements in the sampled fruits, decreasing orders of the determined elements can be formed:

- ✓ Apple: S>>Cu>Zn>Mn>Ni
- ✓ Pear: S>>Cu>Zn>Ni>Mn
- ✓ Peach: S>>Cu>Zn>Mn>Ni
- ✓ Apricot: S>>Cu>Zn>Ni>Mn

The mean concentrations of Zn and especially Cu and S were higher than the concentrations of Mn and Ni in the samples. Maximum concentrations of Cu and S were recorded in the samples of apples, and Zn in the samples of peaches. As can be seen from Table 1, high values of standard deviations of Zn, Cu and S concentrations indicate their large concentration variability in the studied area.
Lăcătuşu and Lăcătuşu (2008) analyzed fruit and vegetables in the areas that are contaminated with heavy metals from mining and industrial activities. Concentrations of Zn in apple and pear are several times lower, while the concentration of Cu are over a hundred times lower than in our study [4]. Lower concentrations of Cu, Zn and Ni were also reported by Hamurcu et al. (2010) in samples of the apples that grew in the traffic related sites. However, the concentration of S in the same sampling area was 1449.64±60.97 mg kg^{-1} [6], which is several times more than in our study area. Also, lower concentrations of Cu, Zn, Mn and Ni were recorded in apricot [3] and peach [5].

Table 1. Descriptive analysis of the concentration of Mn, Ni, Zn, Cu and S (mg kg^{-1}) in apple, pear, apricot and peach in the studied area

Fruits	Elements				
Apple	**Mn (N=10)**	**Ni (N=6)**	**Zn (N=8)**	**Cu (N=8)**	**S (N=10)**
Range	1.65-19.43	0.52-13.16	2.67-93.82	26.79-414.34	197.30-1361.40
Mean ± SD	4.49±5.31	4.39±4.96	43.29±32.97	163.13±125.98	450.83±344.63
Pear	**Mn (N=10)**	**Ni (N=8)**	**Zn (N=7)**	**Cu (N=9)**	**S (N=10)**
Range	1.90-4.82	0.05-8.02	4.94-80.45	10.38-375.87	184.90-431.30
Mean ± SD	2.99±0.89	4.14±3.05	31.11±29.52	94.06±122.14	271.19±72.15
Peach	**Mn (N=6)**	**Ni (N=4)**	**Zn (N=4)**	**Cu (N=5)**	**S (N=6)**
Range	2.06-6.17	0.05-2.85	13.30-75.88	3.49-301.72	204.40-468.90
Mean ± SD	3.46±1.59	1.26±1.16	50.27±30.94	135.61±132.56	348.35±104.12
Apricot	**Mn (N=3)**	**Ni (N=3)**	**Zn (N=3)**	**Cu (N=3)**	**S (N=3)**
Range	4.08-5.53	8.95-9.73	1.43-51.97	6.50-183.61	136.60-458.80
Mean ± SD	4.58±0.83	9.37±0.51	23.69±25.80	95.43±88.56	305.33±161.64

N-number of samples

Figure 2 shows a cluster analysis of heavy metals and sulphur in the fruits: (2a) apples, (2b) pears, (2c) peach and (2d) apricot.

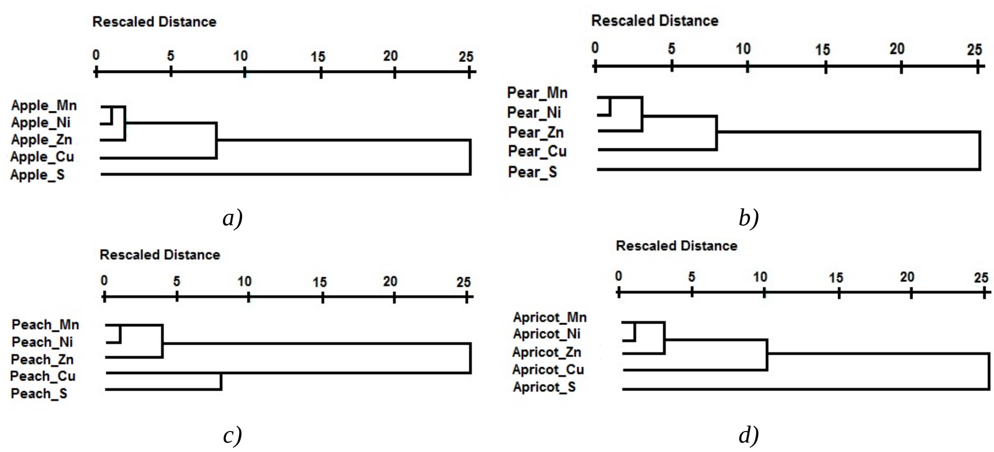

Figure 2. Cluster analysis of heavy metals and sulphur in the fruits: (a) apple, (b) peers, (c) peach and (d) apricot

As can be seen, the elements Mn, Ni and Zn are grouped in a cluster, regardless of the type of fruit, compared to Cu and S. The exception is the creation of another cluster consisting of Cu and S in the samples of peach (Fig. 2c). The large differences in the concentrations of Cu and S compared to other elements in the fruits resulted in their grouping into a separate cluster.

Apart from industry, all these elements in the surrounding area can appear from artificial fertilisers and pesticides. However, such high concentrations of S and Cu are obviously a consequence of the vicinity of the mining and metallurgy complex. Compared to the results which were obtained by other authors it can be concluded that fruits which are originally from our region contain higher concentrations of the studied elements [10,11].

5. CONCLUSIONS

The optimum content of the elements (Cu, Mn, Zn, Ni, S) is essential for proper development of plants. However, high concentrations of these elements can be toxic to plants. Seasonal fruit is a source of nutrients, and may contain toxic elements. In the samples of fruit that was collected in the Bor municipality near the mining and metallurgy complex, average concentrations of Cu and S were higher than the other studied elements. Such high concentrations of these elements are a consequence of the vicinity of the copper smelter, and the use of agricultural chemicals. The grouping of Cu and S into separate clusters indicate their high concentrations.

6. ACKNOWLEDGEMENT

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