Copper and Nickel Determination in Grape Extract Cultured around Marvast City, Yazd

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ABSTRACT

Background: One of the most critical problems in the field of water and food pollution is the heavy metal pollution. Agricultural products are exposed to this type of contamination through wastewater; industrial activity and population pollutions are also in its area. Since the plant in the affected areas can directly enter heavy metals into the food chain, so, it is important to check their level of contamination. The purpose of this study was to monitor distribution of copper and nickel in the grape cultured in the farms around Marvast in Yazd province. Methods: All chemicals were of analytical grade. In order to determine the level of copper and nickel in grape extracts produced from the most important areas in grape production, 7 samples of grape were taken from these geographic regions. After grinding and homogenizing of samples, the concentration of nickel and copper, heavy metals were measured by atomic absorption spectrometer. The obtained results were analyzed through SPSS software based on statistical methods. Results: The mean value of copper and nickel were 26.4 ± 3.1 and 12.3 ± 1.5 μg/kg, respectively. According to the obtained results and their comparison with standards, different amounts of these metals were observed in all samples, however, the highest amount of these metals was observed in one sample. Conclusions: Concentrations of heavy metals in samples from different regions were lower than the maximum allowable concentration of copper and nickel. Although, the amount of these metals in one sample, known as pollution indicator, suggested that this area can be exposed to both.

Keywords: Copper; Nickel; Grape; Marvast city

Introduction

Sometimes plants are used as indicators of ecosystem health (Temple et al., 2012). Fruits and vegetables are important part of human diet. Concentration of heavy elements in these crops is then major factors to recognize healthy foods. Plants’ pollution from heavy metals can be caused by effluent fertilizer and pesticides (Atafar et al., 2010, Azenha and Vasconcelos, 2000a). Fruits and vegetables’ growth environment (soil, air, nutrients) is the main source of heavy metals, plants absorb them via their roots or leaves (Alloway, 1990).
Plants’ uptake and bioaccumulation of heavy metals depends on factors such as climate, atmospheric sediments, soil, heavy metal concentrations in soil, and their growth nature (Moore and Luoma, 1990). Metals are transported into grape plants via root absorption and accumulate into their different parts including the grain (Golia et al., 2008). Mobility of metal ions and its absorption by plant (from root to leaf) is under the influence of soil and soil pH’s physicochemical properties (Antionious and Kochhar, 2009). The final consequence of such accumulation is increase of heavy metals in the fruit. Because of Cu (45–98%) and Ni (16–75%) high gastrointestinal absorption, continuous consumption of fruits with elevated concentrations of them causes chronic poisoning, depending on the type of fruit (Azenha and Vasconcelos, 2000b).

Human health has been at risk by consuming more fruits and vegetables contaminated with heavy metals such as Ni and Cu (Angelova et al., 1999). Cu is a trace element that is essential for human body and biochemical. High amount of Cu causes kidney damage, hypertension, mutagenicity, and carcinogenicity, while overdoses of Ni cause respiratory system, nerve, and heart damage. The maximum allowable concentration of Cu and Ni in adults’ diet should not exceed 10 and 5 mg per kg, respectively (Nunes et al., 2011). The purpose of this study was to monitor distribution of copper and nickel in the grape cultivated in the farms around Marvast in Yazd province.

Materials and Methods

Study design and sampling: This cross-sectional study was carried out in October 2016. 7 samples of grape were collected from all farms of Marvast city of Yazd province in the center of Iran during the fruit production season. In sampling, seedless grapes were taken three times from each region in a month (6 samples per month for 7 region 21 samples). From each region, about 1 kg of grape was collected, placed in a plastic bag, and transported to the laboratory.

Measurements: To exclude possibility of contamination with trace elements, all glasswares were previously washed with 1% of nitric acid and rinsed with distilled water thoroughly. All chemicals were analytical grade and used without any purification. The Cu$^{2+}$ and Ni$^{2+}$ 100-ml stock solutions were prepared by dissolving appropriate amounts of CuSO$_4$·5H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O in distilled water by volumetric flasks. The standard solutions were prepared by diluting its stock solution for each element.

Grape samples were separately washed 3 times, rinsed with distilled water, and crushed in a mill. After grinding and homogenizing, the suspensions were filtrated and centrifuged to obtain a clear solution. The resulting solution was placed into the 105 °C oven for 48 hours to dry completely. One g of each dried sample was weighted by an accurate balance and acid digestion was carried out for each sample according to standard methods. Ni and Cu concentrations were measured 3 times in each sample by atomic absorption spectrometer.

Data analysis: The results were expressed as mean ± SD by using SPSS software (SPSS Inc., Chicago, IL, USA). Differences among groups’ mean scores were determined by independent sample t-test while the significance level was set at P-value < 0.05. For data certification, the analysis of standard solutions provided quality control of the measurements.

Results

The Cu values ranged from 20.6 to 44.1 μg/kg with a mean value of about 26.4 ± 3.1 μg/kg. The Ni values also varied from 10.1 to 21.4 μg/kg with a mean value of 12.3 ± 1.5 μg/kg. The measured elemental concentrations in 3 samples of red grape and 4 samples of white grape as well as their standard errors are presented in Table 1.

The comparison of concentrations of two heavy metals (Cu and Ni) in the studied area are presented in Figure 1.
Regression analysis was applied to investigate the relationship between the variables. For analysis, two variables from each set were chosen (concentration of Cu and Ni). As it can be seen from the following equation, canonical correlation between total elemental concentrations was significant:

$$C_{Ni} = 1.976 \times C_{Cu} + 2.015; \quad R^2 = 0.983; \quad F = 1294$$

A strong positive correlation was found between elemental concentrations of the samples ($R^2=0.983$). These two variables explain the whole variability of the data set (100% variance extracted).

**Discussion**

Due to their toxic nature, existence of heavy metals in foods has been remarkably considered. For example, iron, copper, manganese, zinc, and chromium are essential, while nickel, cadmium, and lead are toxic if consumed higher than the permissible level. However, toxic metals transferred through food chain, especially fruits, have not any essential biochemical function in human biology (Fallah et al., 2011). Hence, regular monitoring of heavy metals’ concentration in fruits and vegetables are necessary for human health that was conducted for copper and nickel in the current study.

Differences in grape cultivars’ heavy metals may be due to growth conditions, genetic factors, soil properties, geographical variations, and analytical procedures. Metals are present in foods either naturally or as a result of human activities such as agricultural practices, industrial emissions, car exhausts, or contamination during transforming (Özcan and Juhaimi, 2012). Trace element and heavy metal pollution levels arising from natural and industrial wastes were recorded from all sampling places. Although in low levels, but Ni and Cu existed in grape extract samples existed (Table 1) which was due to the long term application of fungicide. According to Figure 1, the mean concentration of Cu in the grape juice from the Shahid Mahalati was twice greater than the mean values. The concentrations of all other samples were

### Table 1. Mean ± SD of measured heavy metal concentrations

<table>
<thead>
<tr>
<th>Regions</th>
<th>Cu (µg/kg)</th>
<th>Ni (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Khomeini Dasht</td>
<td>10.1 ± 2.1</td>
<td>10.1 ± 2.1</td>
</tr>
<tr>
<td>Ahmand Abad Bala</td>
<td>24.3 ± 1.9</td>
<td>10.3 ± 3.2</td>
</tr>
<tr>
<td>Ahmand Abad Paeen</td>
<td>23.5 ± 1.2</td>
<td>10.6 ± 2.6</td>
</tr>
<tr>
<td>Shahid Mahalati</td>
<td>44.1 ± 2.3</td>
<td>21.4 ± 4.1</td>
</tr>
<tr>
<td>Mehdi Abad</td>
<td>20.6 ± 1.8</td>
<td>10.7 ± 3.5</td>
</tr>
<tr>
<td>Sargheshmah</td>
<td>27.3 ± 1.6</td>
<td>11.4 ± 2.4</td>
</tr>
<tr>
<td>Hossein Abad</td>
<td>23.2 ± 0.9</td>
<td>10.8 ± 3.1</td>
</tr>
</tbody>
</table>

**Figure 1.** Amount of two heavy metals in grape samples.
marginally similar. Higher Ni values were determined in samples taken from the Shahid Mahalati region.

Conclusion
More studies are required to explain about the real amount of grape heavy metals in an area. This research investigated the presence of Ni and Cu metals in grape extracts. Furthermore, the overall results of this study suggested a low concentration of copper and nickel in all samples.

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Author contributions
Salmani MH participated in designing the study and editing the manuscript. Shirvani N and Shekari Z performed sampling, carried out the experiments, and composed the manuscript. All authors read and approved the final manuscript.

Conflict of Interest
The authors declare that they have no conflict of interest.

References