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Comparative Study of Heavy Metal Content in Bilbery and Raspery from Farm Cuture

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Abstract

The aim of this study is testing the accumulation of heavy metals in bilberries (*Vaccinium myrtillus*) and raspberries (*Rubus idaeus*), focusing on their variability, bioaccumulation patterns, and potential health risks. Both fruits are known for their nutritional benefits but are also capable of absorbing heavy metals like cadmium (Cd), lead (Pb), and zinc (Zn) from their environments. The study reveals that titanium (Ti) and iron (Fe) are the most abundant metals in both fruits, with bilberries showing higher levels of manganese (Mn), cadmium, and silver (Ag), while raspberries exhibit greater concentrations of zinc, chromium (Cr), and tin (Sn). The results highlight species-specific differences in metal uptake, likely influenced by environmental factors such as soil composition and contamination levels. Toxic metals like cadmium and silver are more prevalent in bilberries, raising safety concerns for their consumption. Pearson correlation analyses and clustering patterns reveal relationships between various metals, indicating shared environmental pathways or distinct accumulation mechanisms.

Keywords: accumulation, contamination, correlation, pollution.

1. Introduction

Environmental pollution, particularly soil contamination with heavy metals, poses significant risks to human health and ecosystems. Fruits like bilberries (*Vaccinium myrtillus*) and raspberries (*Rubus idaeus*), known for their health benefits, can accumulate heavy metals from contaminated soils, potentially compromising their safety for consumption. Studies have shown that these berries can absorb metals such as cadmium (Cd), lead (Pb), and zinc (Zn) from the soil, with varying accumulation patterns depending on the metal and plant species [4, 6, 8]

For instance, research indicates that bilberries tend to accumulate higher levels of zinc, followed by copper (Cu) and lead, while raspberries show a different accumulation order [1, 5, 7]. The transfer of heavy metals from soil to plant tissues is influenced by factors such as soil metal concentration, plant species, and environmental conditions. Higher soil metal concentrations generally lead to increased accumulation in plant tissues, though the transfer coefficient may decrease as soil contamination intensifies [2, 3, 4].

Understanding the extent of heavy metal accumulation in these berries is crucial, as consumption of contaminated fruits can pose health risks. Regular monitoring of heavy metal levels in both soil and fruit is essential to ensure food safety and protect public health. This study aims to evaluate the concentrations of various heavy metals in bilberries and raspberries, assess the variability, and explore the correlations between soil and fruit metal contents to better understand the bioaccumulation patterns in these berries.

2. Material and Method

Bilberry (*Vaccinium myrtillus*) and raspberry (*Rubus idaeus*) samples were collected from two private farms located in mountain area of Bistrița-Năsăud County. Five replicates of each fruit type and soil sample were collected to ensure statistical reliability. The sampling sites were selected. The fruits were carefully cleaned with deionized water to remove surface contaminants, air-dried at room temperature, and homogenized using a mechanical grinder to obtain a fine powder for analysis.

Soil samples were air-dried, sieved through a 2-mm mesh to remove debris, and homogenized to ensure uniformity. The concentrations of heavy metals (e.g., Ti, Fe, Mn, Cr, Zn, Cd, Ag, Sn, Cu, Sb) in fruit and soil samples were determined using X-ray fluorescence (XRF) spectrometry. This non-invasive technique provided precise measurements of metal content without requiring chemical digestion. The XRF instrument was calibrated using certified reference materials, and quality control was ensured through the inclusion of blanks and duplicates in the analysis.

Basic descriptive statistics, including mean (X), minimum (Min.), maximum (Max.), standard deviation (s), and coefficient of variation (CV%), were calculated for each metal in both fruit and soil samples to evaluate the variability and concentration. Simple Pearson correlation coefficients were computed to examine the relationships between heavy metal concentrations in fruits.

3. Results and Discussions

The data presented in Table 1 highlights the variability and concentration of heavy metals in blueberries, providing insights into their distribution and potential sources. Titanium (Ti) and iron (Fe) exhibit the highest average concentrations, with low coefficients of variation (CV%) at 1.09% and 2.71%, respectively, indicating consistent levels across the samples and suggesting stable environmental availability. Manganese (Mn), while lower in concentration, shows moderate variability (5.36%), reflecting potential environmental heterogeneity.

Chromium (Cr), tin (Sn), and copper (Cu) demonstrate moderate average concentrations with relatively higher variability, as shown by CV values between 7.89% and 9.55%, indicating some differences in uptake influenced by soil composition or environmental factors. Zinc (Zn) and cadmium (Cd) display similar average concentrations, but cadmium, a toxic metal, is of particular concern due to its bioaccumulation potential and health implications.

Vanadium (V), silver (Ag), and nickel (Ni) exhibit higher variability, as seen from their CV values of 12.06%, 18.56%, and 15.77%, respectively, reflecting significant differences in their distribution across samples, potentially due to localized contamination or environmental variability. Gallium (Ga), though present in very low concentrations, shows a relatively consistent distribution with a CV of 8.79%, indicating less variability.

Table 1. Basic statistics for heavy metals from blilberries

Heavy metal	N	X	Min.	Max.	s	CV%
Ti	5	68.14	67.00	69.00	0.74	1.09
Fe	5	41.28	40.00	43.00	1.12	2.71
Mn	5	14.12	13.00	15.00	0.76	5.36
Cr	5	10.16	9.00	11.20	0.93	9.17
Sn	5	7.60	7.00	8.40	0.60	7.89
Cu	5	6.68	5.90	7.50	0.64	9.55
Zn	5	5.66	5.00	6.20	0.50	8.80
V	5	6.14	5.00	7.00	0.74	12.06
Cd	5	4.70	4.00	5.10	0.44	9.27
Ag	5	4.06	3.00	5.00	0.75	18.56
Ni	5	2.44	2.00	3.00	0.38	15.77
Ga	5	1.37	1.20	1.50	0.12	8.79

n-number of replicates; X-average; s-standard deviation; CV-coefficient of variation.

The high variability observed in toxic metals like silver and nickel emphasizes the need for careful monitoring, as their inconsistent distribution could pose localized health risks. The data suggest a mix of stable and variable metal concentrations in blueberries, likely influenced by environmental factors and metal-specific properties.

In raspberries, iron (Fe) and titanium (Ti) exhibit the highest average concentrations with low coefficients of variation (CV%) at 2.05% and 1.66%, respectively, suggesting consistent levels and stable environmental availability. Chromium (Cr) and antimony (Sb) show moderate concentrations with relatively low variability (4.69% and 4.14%, respectively), indicating their stable presence in the samples (Table 2). Manganese (Mn) and zinc (Zn) display higher variability, with CVs of 7.10% and 9.89%, respectively, reflecting environmental or uptake differences between samples. Zinc, an essential element, shows higher variability than Mn, possibly due to localized soil differences or contamination sources. Tin (Sn), copper (Cu), and cadmium (Cd) exhibit moderate concentrations with variability ranging from 5.09% to 7.93%, indicating some environmental heterogeneity or differences in plant uptake mechanisms.

Silver (Ag), strontium (Sr), and gallium (Ga) show lower average concentrations with higher variability, particularly Sr and Ga, which have CVs of 10.28% and 9.01%, respectively.

This variability may point to localized environmental factors or differences in the bioavailability of these metals. The presence of cadmium, a toxic metal, requires attention due to its potential health risks, even though its variability is moderate.

The data show that raspberries generally exhibit stable levels of most metals, particularly Fe and Ti, while metals like Zn, Sr, and Ga display higher variability.

This variability suggests the influence of environmental factors, soil composition, and metal-specific properties on their accumulation in raspberries.

Table 2. Basic statistics for heavy metals from raspberry

Heavy metal	N	X	Min.	Max.	s	CV%
Fe	5	55.60	54.00	57.00	1.14	2.05
Ti	5	56.16	55.00	57.20	0.93	1.66
Cr	5	16.06	15.00	17.00	0.75	4.69
Sb	5	14.66	14.00	15.50	0.61	4.14
Mn	5	11.94	11.00	13.00	0.85	7.10
Zn	5	12.22	10.20	13.10	1.21	9.89
Sn	5	10.62	10.00	11.20	0.54	5.09
Cu	5	7.54	7.00	8.00	0.46	6.05
Cd	5	5.50	5.00	6.00	0.44	7.93
Ag	5	4.62	4.00	5.00	0.38	8.16
Sr	5	1.67	1.50	1.90	0.17	10.28
Ga	5	0.80	0.70	0.90	0.07	9.01
Br	5	0.37	0.25	0.50	0.10	26.34
Se	5	0.19	0.15	0.24	0.04	18.08

n-number of replicates; X-average; s-standard deviation; CV-coefficient of variation.

The Pearson correlations show the relationships between the concentrations of heavy metals in bilberries, revealing distinct patterns of association that reflect similarities or differences in their behavior and accumulation (Table 3.

Titanium (Ti) shows strong positive correlations with several metals, including vanadium (V, r = 0.78), chromium (Cr, r = 0.76), and copper (Cu, r = 0.75), suggesting that these metals may share environmental pathways or similar uptake mechanisms in bilberries. Iron (Fe) exhibits strong correlations with vanadium (V, r = 0.92), nickel (Ni, r = 0.99), and silver (Ag, r = 0.97), indicating a significant relationship among these metals, potentially due to similar environmental or soil influences.

Manganese (Mn) stands out with predominantly weak or negative correlations with most other metals, such as iron (r = -0.50) and vanadium (r = -0.21), reflecting distinct accumulation patterns that may be influenced by specific environmental or biological factors unique to manganese. Chromium (Cr) shows a very strong correlation with zinc (Zn, r = 0.97) and silver (Ag, r = 0.94), indicating a potential shared source or similar mobility in the environment.

Tin (Sn) and copper (Cu) are closely related (r = 0.98), reflecting nearly identical accumulation behavior, which could be attributed to similar chemical properties or environmental availability. Zinc (Zn) correlates strongly with chromium (Cr, r = 0.97) and silver (Ag, r = 0.89), suggesting overlapping environmental or biological pathways.

Cadmium (Cd) exhibits moderate correlations with other metals, such as tin (r = 0.54) and silver (r = 0.66), while showing stronger relationships with gallium (Ga, r = 0.95). The high correlation between gallium and cadmium suggests that they might co-occur due to specific soil conditions or contamination sources.

Vanadium (V) demonstrates strong positive correlations with several metals, such as silver (Ag, r = 0.97), nickel (Ni, r = 0.91), and gallium (Ga, r = 0.79), suggesting shared environmental pathways or soil influences. Silver (Ag) and nickel (Ni) are closely related (r = 0.97), further supported by their strong links to other metals like vanadium and iron.

Metals strong correlated, such as zinc and chromium or silver and nickel, indicate shared environmental sources or similar mobility, while weak or negative correlations, such as manganese with iron, highlight distinct accumulation behaviors.

Table 3. The simple Pearson correlations between heavy metals identified bilberries

Issue	Ti	Fe	Mn	Cr	Sn	Cu	Zn	V	Cd	Ag	Ni	Ga
Ti	1.00	0.51	0.45	0.76	0.61	0.75	0.74	0.78	0.67	0.70	0.52	0.47
Fe	0.51	1.00	-0.50	0.86	-0.24	-0.05	0.78	0.92	0.59	0.97	0.99	0.69
Mn	0.45	-0.50	1.00	-0.05	0.71	0.67	-0.01	-0.21	-0.12	-0.29	-0.47	-0.42
Cr	0.76	0.86	-0.05	1.00	-0.04	0.15	0.97	0.87	0.44	0.94	0.90	0.41
Sn	0.61	-0.24	0.71	-0.04	1.00	0.98	0.03	0.15	0.54	-0.03	-0.26	0.28
Cu	0.75	-0.05	0.67	0.15	0.98	1.00	0.19	0.33	0.64	0.15	-0.08	0.38
Zn	0.74	0.78	-0.01	0.97	0.03	0.19	1.00	0.81	0.44	0.89	0.85	0.39
V	0.78	0.92	-0.21	0.87	0.15	0.33	0.81	1.00	0.80	0.97	0.91	0.79
Cd	0.67	0.59	-0.12	0.44	0.54	0.64	0.44	0.80	1.00	0.66	0.54	0.95
Ag	0.70	0.97	-0.29	0.94	-0.03	0.15	0.89	0.97	0.66	1.00	0.97	0.69
Ni	0.52	0.99	-0.47	0.90	-0.26	-0.08	0.85	0.91	0.54	0.97	1.00	0.63
Ga	0.47	0.69	-0.42	0.41	0.28	0.38	0.39	0.79	0.95	0.69	0.63	1.00

In raspberries, iron (Fe) shows a strong positive correlation with tin (Sn, r = 0.83) and selenium (Se, r = 0.68), suggesting potential co-accumulation or shared environmental sources. However, Fe exhibits moderate to weak negative correlations with other metals, such as manganese (Mn, r = -0.16) and cadmium (Cd, r = -0.45), indicating distinct behaviors and uptake mechanisms for these metals. Titanium (Ti) demonstrates strong positive correlations with chromium (Cr, r = 0.94), antimony (Sb, r = 0.97), and manganese (Mn, r = 0.94), suggesting a shared environmental pathway or similar accumulation dynamics in raspberries. Its high correlation with gallium (Ga, r = 0.86) further supports the idea of related mobility or availability in the soil (Table 4).

Chromium (Cr) and manganese (Mn) are highly correlated (r = 0.95), indicating their consistent co-occurrence, potentially due to similar environmental factors influencing their distribution. Chromium also has strong correlations with antimony (Sb, r = 0.83) and gallium (Ga, r = 0.98), suggesting related pathways or soil sources for these metals. Zinc (Zn) exhibits moderate correlations with manganese (Mn, r = 0.75) and copper (Cu, r = 0.79), reflecting potential partial overlap in their accumulation mechanisms. However, its weak correlations with several metals, such as cadmium (Cd, r = -0.19), suggest variability in its behavior depending on environmental conditions. Tin (Sn) shows strong correlations with selenium (Se, r = 0.97) and silver (Ag, r = 0.76), indicating possible shared pathways or chemical affinities. Selenium's high correlation with tin suggests specific bioaccumulation dynamics in raspberries. Copper (Cu) demonstrates strong relationships with manganese (Mn, r = 0.96) and chromium (Cr, r = 0.89), reflecting its association with metals that share biological or environmental pathways. However, its weak or negative correlations with other metals, such as tin and selenium, highlight unique aspects of its behavior. Silver (Ag) correlates strongly with antimony (Sb, r = 0.74) and selenium (Se, r = 0.73), suggesting a tendency to co-accumulate with these metals, while its weak relationship with strontium (Sr, r = -0.05) reflects distinct accumulation mechanisms. Strontium (Sr) demonstrates weak to moderate positive correlations with most metals, such as cadmium (Cd, r = 0.65), but shows negative correlations with selenium (Se, r = -0.41) and iron (Fe, r = -0.71), suggesting variability in its environmental or biological pathways. Gallium (Ga) shows strong positive correlations with chromium (Cr, r = 0.98), antimony (Sb, r = 0.72), and titanium (Ti, r = 0.86), indicating its consistent association with these metals, potentially due to shared environmental factors.

Certain metals, such as chromium, manganese, and titanium, share similar environmental or biological pathways, while others, like cadmium and strontium, show distinct accumulation behaviors.

Table 4. The simple Pearson correlations between heavy metals identified raspberries

Issue	Fe	Ti	Cr	Sb	Mn	Zn	Sn	Cu	Cd	Ag	Sr	Ga	Br	Se
Fe	1.00	0.12	-0.11	0.30	-0.16	-0.08	0.83	-0.06	-0.45	0.61	-0.71	-0.24	0.31	0.68
Ti	0.12	1.00	0.94	0.97	0.94	0.64	0.16	0.88	0.25	0.73	0.22	0.86	0.84	0.16
Cr	-0.11	0.94	1.00	0.83	0.95	0.51	0.11	0.89	0.56	0.68	0.46	0.98	0.64	0.18
Sb	0.30	0.97	0.83	1.00	0.87	0.70	0.21	0.83	0.02	0.74	0.07	0.72	0.93	0.15
Mn	-0.16	0.94	0.95	0.87	1.00	0.75	-0.10	0.96	0.38	0.57	0.53	0.92	0.79	-0.07
Zn	-0.08	0.64	0.51	0.70	0.75	1.00	-0.38	0.79	-0.19	0.22	0.44	0.45	0.88	-0.50
Sn	0.83	0.16	0.11	0.21	-0.10	-0.38	1.00	-0.01	0.10	0.76	-0.50	0.04	0.06	0.97
Cu	-0.06	0.88	0.89	0.83	0.96	0.79	-0.01	1.00	0.36	0.63	0.59	0.87	0.82	-0.03
Cd	-0.45	0.25	0.56	0.02	0.38	-0.19	0.10	0.36	1.00	0.29	0.65	0.68	-0.21	0.29
Ag	0.61	0.73	0.68	0.74	0.57	0.22	0.76	0.63	0.29	1.00	-0.05	0.61	0.60	0.73
Sr	-0.71	0.22	0.46	0.07	0.53	0.44	-0.50	0.59	0.65	-0.05	1.00	0.59	0.12	-0.41
Ga	-0.24	0.86	0.98	0.72	0.92	0.45	0.04	0.87	0.68	0.61	0.59	1.00	0.53	0.14
Br	0.31	0.84	0.64	0.93	0.79	0.88	0.06	0.82	-0.21	0.60	0.12	0.53	1.00	-0.07
Se	0.68	0.16	0.18	0.15	-0.07	-0.50	0.97	-0.03	0.29	0.73	-0.41	0.14	-0.07	1.00

The illustration of the comparative content of heavy metals in bilberries and raspberries shows differences in their accumulation patterns (Fig. 1). Titanium (Ti) and iron (Fe) are the most abundant metals in both fruits, with higher concentrations observed in bilberries for titanium, while raspberries contain slightly more iron. This suggests differing environmental availability or uptake efficiencies for these metals between the two fruits.

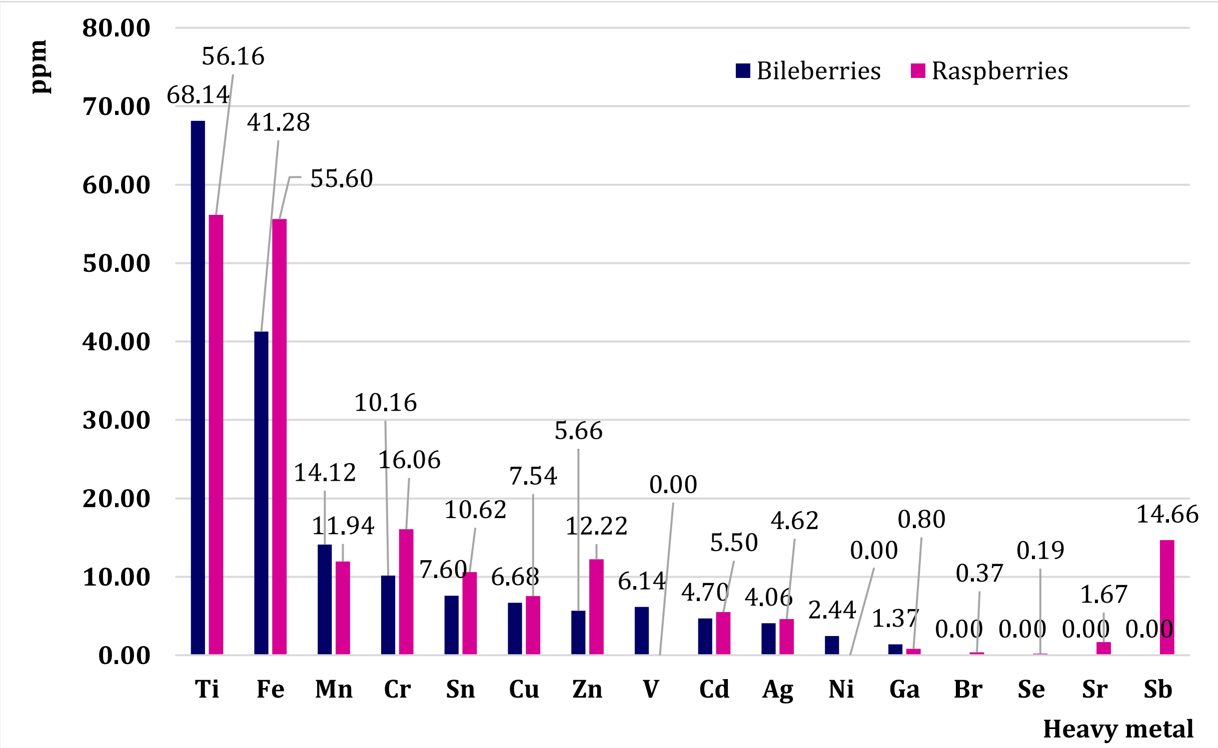

Figure 1. Comparative content of heavy metals in bilberries and raspberries

Manganese (Mn) is more prevalent in bilberries than in raspberries, indicating a greater capacity for manganese accumulation in bilberries or higher soil availability in their growth environments. Chromium (Cr), tin (Sn), and copper (Cu) show higher concentrations in raspberries, reflecting distinct environmental or physiological factors influencing their uptake. Zinc (Zn) exhibits a notable difference, with raspberries showing approximately double the concentration compared to bilberries, suggesting significant variability in zinc uptake or availability. Cadmium (Cd) and silver (Ag), which are toxic metals, are more concentrated in bilberries than in raspberries, raising potential concerns regarding their consumption. Metals such as nickel (Ni), gallium (Ga), and strontium (Sr) are detected at low levels in both fruits, with raspberries generally showing higher levels of gallium and strontium. Antimony (Sb) is present only in raspberries, while vanadium (V) and bromine (Br) are detected exclusively in bilberries, indicating fruit-specific metal accumulation patterns.

4. Conclusions

The comparative analysis of heavy metal content in bilberries and raspberries reveals distinct accumulation patterns influenced by environmental and physiological factors. Titanium (Ti) and iron (Fe) are the most abundant metals in both fruits, with bilberries showing higher titanium levels and raspberries slightly exceeding iron content, indicating varying uptake efficiencies or environmental availability. Bilberries exhibit higher concentrations of manganese (Mn) and toxic metals such as cadmium (Cd) and silver (Ag), raising potential concerns regarding their safety for consumption. Raspberries, on the other hand, contain significantly higher levels of zinc (Zn), chromium (Cr), tin (Sn), and copper (Cu), suggesting differential accumulation mechanisms or soil composition in their growth environments. The exclusive presence of antimony (Sb) in raspberries and vanadium (V) and bromine (Br) in bilberries highlights species-specific metal uptake and distribution. These findings emphasize the need for regular monitoring of heavy metal content in fruits, particularly in species prone to accumulating toxic elements. The observed variability shows the role of environmental factors, such as soil composition and contamination, in shaping the metal profiles of bilberries and raspberries.

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