Assessment of Relationship Between Geochemical Fractions of Barium in Soil of Cherry Orchards and Plant Barium Uptake and Determination by Inductively Coupled Plasma Optical Emission Spectrometry

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INTRODUCTION

Trace elements exist at different concentrations and in different geochemical fractions based on soil parent material and environmental factors. Information is available about the environmental impact, potential sources, and mobility of the trace metals with already known geochemical fractions. Previous studies have assessed the potential impact of trace metals on the environment, mostly focused on their total concentrations (1-5). However, it is generally accepted that assessment of the total concentration may not reveal distinctive effects of trace metals on the environment. This could be explained since solubility, mobility, and bioavailability of trace metals largely depend on their chemical forms; assessment of only total concentration may be insufficient in assessing the potential toxicity and impact of the trace metals on the environment. For this reason, speciation methods are used to reach valuable information about the bioavailability and toxicity of trace metals (6).

Barium is a metal used in medical analysis and in the production of ceramics, painting, monitors, as well as for cigarettes-tobacco,

ABSTRACT

This study was conducted to investigate the relationship of geochemical fractions of Ba in soils of cherry orchards and in plant Ba uptake. The levels of Ba in the soil samples were determined after sequential extraction procedure and analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). At the same time, the levels of Ba in cherry leaf samples were determined after a wet digestion procedure by ICP-OES. Soil total Ba concentrations (mean 108.9 $\mu\text{g g}^{-1}$) were found within normal ranges specified for agricultural soils. The Ba concentration in the cherry leaf samples was found in the range of 9.1 $\mu\text{g g}^{-1}$ to 20.6 $\mu\text{g g}^{-1}$. Sequential extraction revealed that Ba existed in highly mobile phases (42%), which are attributed to anthropogenic sources as well as to decomposition of soil parent material. The experimental data were subjected to hierarchical cluster analysis to assess the relationship between the Ba concentration of each fraction and the leaf Ba contents. A significant correlation was observed between the leaf Ba concentrations and the acid soluble fraction.

tors (8, 9). The total safe dietary intake of barium is 0.75 mg day⁻¹ with nutrients at the level of 70-80% and drinking water at the rate of 20% (9). For WHO, EPA and OSHA there are barium standards for drinking water and in breathing air. These standards are categorized as 0.7 mg/L for WHO and 2 mg/L for U.S. EPA for drinking water and 0.5 milligrams of soluble barium compounds per cubic meter for air.

Barium (Ba) is classified among trace elements and is a common alkaline-earth metal, found all over the earth's crust. High soil Ba concentrations are mostly related to limestone, feldspar, and shale deposits (10). Although Ba is known as the 14th most abundant element on the earth, a relatively low number of studies have investigated the formation of Ba in soils (11). There are many studies in the literature on trace metal contents in plants (12-15). No known biological functions of Ba have been published, but it is widely found in plants. Despite the low number of studies on Ba, it was reported that high accumulation levels result in toxicity in plants (16). Therefore, further studies on Ba in soils and plants will make significant contributions to this question.

Today, the analysis of samples following a digestion procedure can be performed using single-element spectroscopic techniques, such as FAAS and GFAAS, to multi-

pyrotechnics, and petroleum (7). It has been reported that Ba could enter the human body via oral-digestion, inhalation, or dermal vec-

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element analysis by ICP-OES and ICP-MS (17) for a large number of analytes in a relatively short time, allowing for larger sample characterization. ICP-OES offers simultaneous elemental analysis with relatively low detection limits and easy access (18, 19) compared to FAAS and GFAAS.

According to our literature research, no study has reported on the Ba concentration of cherry garden soil samples after sequential extraction by inductively coupled plasma optical emission spectrometry. Cherry is among the most significant stone-fruit species in Turkey. Since it is among commercially valuable fruit species, it is grown in different geographies and ecologies. In the Çanakkale province, cherry cultivation is practiced over a 1700 ha land area with an annual production of 20,000 tons (20). Therefore, in this study, the geochemical fractions and mobility of Ba in the soils of cherry orchards were investigated and the relationships between different fractions of Ba and plant uptakes are put forth.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Optima™ 8000 Model inductively coupled plasma optic emission spectrophotometer (PerkinElmer, Inc., Shelton, CT, USA) was used for the determination of the Ba. The instrument was optimized daily before measurements and operated as recommended by the manufacturer. The instrumental parameters are listed in Table I.

Reagents and Standard Solutions

All reagents and chemicals used were of analytical grade (Merck, Germany). Doubly distilled deionized water was used throughout the experiments (TKA-GenPure, Germany). ICP-OES barium measurements were performed

without using the internal standard. The stock standard solution (1000 mg L⁻¹) of Ba was obtained from Merck, Germany. Working standards (0.05 - 5 mg L⁻¹) of the Ba were prepared from related dilution of the stock standard solutions with distilled water.

Research Site and Sampling

Some of the orchards in the town of Lapseki in the Çanakkale province (Turkey) were selected as the research site for this study. Cherry orchards were generally established over the alluvial flood plains of the town. The research site is mostly composed of flat or almost flat terrain. Soil samples were taken from the 0-30 cm upper soil profile. Three different points were selected in each orchard (15 orchards), and the soil samples taken from the mid-point of four cherry trees. Then, these soil samples were mixed, and a composite sample representing the entire orchard was obtained. Non-metallic tools were used in soil sampling, and all samples were brought to the laboratory in polyethylene containers. The samples were air-dried at room temperature (20-25 °C) and passed through a 2 mm sieve. The soil texture, pH, and electrical conductivity of these samples were established. A portion of the samples was passed through a 105 µm sieve and homogenized with a mortar. In addition, these samples were used to determine

the soil organic matter content, calcium carbonate content, and Ba content.

In the selected orchards, 25 leaf samples were also taken from each of the four trees surrounding each soil sampling point. Then, the samples taken from the three different locations were mixed to get a composite sample. The leaf samples were washed with deionized water and dried at 65 °C for 48 hours until a constant weight was reached. The dried leaves were then ground in an agate mortar, homogenized, and made ready for analysis.

Analysis

Soil reaction (pH) was measured at 1 : 2.5 soil : water suspension with a glass-electrode pH-meter (21). Soil electrical conductivity (EC) was measured again at 1 : 2.5 soil : water suspension with an EC-meter (22). Soil texture was measured using the hydrometer method in accordance with the principles specified by Bouyoucos (23). Soil organic matter (SOM) content was measured using the dichromate oxidation procedure. Soil calcium carbonate (CaCO₃) was measured with a calcimeter (ILDAM Laboratory Equipment, Turkey) through acidification of the soil samples and measuring the CO₂ volume.

The Ba concentration of the soil samples was determined by using the wet digestion (aqua regia)

TABLE I
Operating Conditions for PerkinElmer Optima 8000 ICP-OES

RF power	1400 W
Auxiliary argon flow rate	0.2 L min ⁻¹
Plasma gas flow	10 L min ⁻¹
Nebulizer flow	0.8 L min ⁻¹
Nebulizer	Meinhard® Concentric Glass
Spray chamber	Cyclonic
Sample aspiration rate	0.3 mL min ⁻¹
Sample pump rate	20 rpm
Ba wavelength	233.527 nm

method. Modified BCR sequential extraction was used to determine the geochemical fractions of Ba. In this method, four fractions were identified, respectively, as acid soluble (F_1), reducible (F_2), oxidizable (F_3), and residual (F_4) fractions. Detailed information about the BCR sequential extraction method can be found in previous studies (24-26).

About 1 g of dried leaf sample was wet-digested in a mixture using 12 mL HNO_3 (65%) and 6 mL H_2O_2 (35%). The mixture was heated to dryness (about 4-5 mL sample). The digested sample was brought to 25 mL volume with 1M HNO_3 .

The concentrations of Ba extracted from the soil and leaf samples were determined by ICP-OES. The limit of detection of ICP-OES for Ba ($\text{LOD} = 3s$, three times the standard deviation of the blank signals) was $0.008 \mu\text{g g}^{-1}$.

Statistical Analysis

Pearson's correlation analysis was used to determine the correlation between soil characteristics and the different Ba fractions. Similarities between the samples were analyzed through hierarchical cluster analysis. MINITAB-16 statistical software (StatSoft, Inc. Tulsa OK, USA) was used for statistical analysis of the experimental data.

RESULTS AND DISCUSSION

Descriptive Statistics for Soil Characteristics

The geochemical characteristics of the soil samples are summarized in Table II. The soil pH levels were generally neutral (6.69). The electrical conductivity values varied between $326 - 898 \mu\text{S cm}^{-1}$ and did not pose any salinity problems on the soil samples. The soil organic matter content varied between $0.99 - 3.17\%$, with an average value of 1.87% . The soil organic matter levels were generally medium. The

average soil calcium carbonate (CaCO_3) content was 2.62% and thus, the soils were considered as low limy. The soil clay content varied between $9.1 - 16.1\%$, with an average value of 13.2% .

Ba Concentrations of Soil and Leaf Samples

The soil Ba geochemical fractions and the leaf barium concentrations are provided in Table III. The total Ba concentration of the soil samples varied between $88.3 - 123.7 \mu\text{g g}^{-1}$ with an average value of $108.9 \mu\text{g g}^{-1}$. The average Ba content of the earth's crust is $400 \mu\text{g g}^{-1}$, and the Ba content of the upper continental crust is between $250 - 584 \mu\text{g g}^{-1}$ (27). Pais and Jones (28) reported the general Ba content of soils at $100 \mu\text{g g}^{-1}$. Thus, the present average value ($104.6 \mu\text{g g}^{-1}$) was slightly higher than the general average of soils ($100 \mu\text{g g}^{-1}$). The Ba content of various plant species varies between

$4 - 50 \mu\text{g g}^{-1}$ (29). In this study, the Ba concentration in the cherry leaf samples was found in the range of $9.1 \mu\text{g g}^{-1}$ to $20.6 \mu\text{g g}^{-1}$. Even though the Ba concentrations determined in the leaf samples are not alarming for agricultural production, it is suggested to monitor Ba in the long run.

Bioavailability, mobility, or immobility of trace elements is generally related to the type of binding of these elements to the soil matrix. Metal mobility and bioavailability of different geochemical fractions are ordered as acid soluble (F_1) > reducible (F_2) > oxidizable (F_3) > residual (F_4) fractions. The average quantity of Ba fractions of the BCR sequential extraction method is presented in Figure 1 as rational distribution. Barium concentrations of different fractions follow the order: F_4 (58%) > F_2 (29%) > F_1 (9%) > F_3 (4%).

With the implementation of the

TABLE II
Geochemical Characteristics of Soil Samples

Sample No.	pH ($\mu\text{S cm}^{-1}$)	EC (%)	CaCO_3 (%)	OM (%)	Clay (%)	Silt (%)	Sand (%)
1	7.02	554	3.44	1.36	9.1	19.9	71.0
2	7.15	513	3.75	0.99	14.1	21.1	64.8
3	6.42	602	2.26	1.21	9.9	14.8	75.3
4	6.56	550	2.41	1.39	14.1	10.5	75.4
5	7.35	573	2.96	1.40	16.1	12.8	71.2
6	6.75	458	2.41	2.44	14.1	14.8	71.2
7	6.36	815	2.18	2.82	13.0	19.0	68.0
8	6.22	624	2.22	3.17	9.9	16.9	73.2
9	7.38	326	2.10	2.47	12.0	13.8	74.3
10	6.18	898	2.70	2.41	13.0	12.8	74.3
11	6.21	458	2.67	2.14	15.2	10.2	74.6
12	6.57	365	2.55	1.85	14.8	12.8	72.4
13	6.86	567	2.20	1.34	14.1	13.4	72.5
14	7.05	718	3.00	1.46	15.0	11.5	73.5
15	6.33	645	2.45	1.58	13.8	10.5	75.7
Min.	6.18	326	2.10	0.99	9.1	10.2	64.8
Max.	7.38	898	3.75	3.17	16.1	21.1	75.7
Mean	6.69	578	2.62	1.87	13.2	14.3	72.5
Sd	0.42	153	0.48	0.66	2.1	3.5	3.0

sequential extraction procedure, Ba was seen to be mostly in the F₄ fraction with about 58% contribution to total metal content. This fraction is highly immobile and corresponds to the lithogenic origin of the metal. Second, Ba was dominant in the F₂ fraction, and the lowest amount was found in the F₃ fraction. While Ba strongly adsorbs on soil Fe-Mn (hydr) oxides (30), it cannot bind strongly to organic ligands (31).

Palumbo et al. (32) indicated that Ba compounded to Mn (hydr) oxides rather than the Fe (hydr) oxides in Fe-Mn nodules. Barium is not a redox-sensitive element, but in soils subjected to changes in redox potential, Ba adsorption or desorption may be influenced by oxidation or reduction of the other redox-sensitive compounds (33, 34). On the other hand, reduction leads to solubility of barium sulfate

supporting greater mobility and bioavailability (35).

Considering the trace metal quantities extracted through the sequential extraction method, the concentrations of the first three fractions (F₁+F₂+F₃) are accepted as potential mobile fractions (36). Potential Ba mobility based on the first three fractions of the soil samples (acid soluble + reducible + oxidizable) was identified as 42% (Figure 1). Since metals are bound to silicates and primary minerals in unpolluted soils, they are basically immobile. However, they are highly mobile and bound to other fractions in contaminated soils (36). The present lower mobile Ba fractions than immobile fractions found in this study indicated parent rock or parent material, since lithogenic-originated trace metals are mostly bound to the soil matrix; in other words, Ba exists in the structure of

silicates. The metals bound to the soil matrix can be released only through severe disintegration and then turn into mobile forms.

Relationships Between Different Fractions of Ba and Soil Property

The Pearson correlation analysis was performed to determine the relationship between soil physico-chemical attributes (pH, organic matter, CaCO₃ content, and clay content) and the Ba concentrations of each fraction. The analysis results are provided in Table IV.

Soil pH is directly related to mobility and bioavailability of the metals. Decrease in soil pH may reduce trace metal adsorption, and mobility may increase through increased competition between H⁺ and dissolved metals for negative surfaces, such as organic matter and clay minerals (26). There was a negative correlation between soil pH and the F₁ fraction ($r = -0.899$). In other words, Ba tended to be more mobile with decreasing pH values. Similarly, it was reported that Ba solubility increased with decreasing pH values (35, 37).

Soil organic matter positively correlated with the F₁, F₂, and F₃ fractions of Ba. There were highly significant correlations, especially between OM and F₃ (the fraction bound to organic matter and sulfur)

TABLE III
Results of BCR Sequential Extraction for Ba
in Soil Samples and in Cherry Leaf Samples ($\mu\text{g g}^{-1}$)

Sample No.	Acid-soluble	Reducible (F ₂)	Oxidizable (F ₃)	Residual (F ₄)	Total (ΣF)	Cherry Leaf
1	7.53	28.70	3.64	48.41	88.28	9.19
2	7.19	29.22	2.84	65.06	104.31	9.06
3	9.66	26.43	3.83	53.13	93.05	17.93
4	8.18	25.24	3.36	56.20	92.99	9.85
5	6.51	31.68	3.48	82.08	123.74	11.27
6	9.77	38.96	5.48	68.71	122.91	17.35
7	11.16	32.87	5.45	47.99	97.48	13.24
8	13.04	37.84	8.15	54.19	113.22	20.58
9	6.15	35.16	5.81	60.49	107.61	10.95
10	11.38	33.36	5.00	52.50	102.23	15.19
11	12.05	29.65	4.23	75.26	121.19	20.35
12	11.57	34.02	3.25	70.39	119.23	20.12
13	9.51	33.58	3.67	67.25	114.01	18.63
14	8.54	32.54	3.98	72.38	117.44	9.62
15	10.24	31.24	4.26	69.65	115.39	19.35
Min.	6.15	25.24	2.84	47.99	88.28	9.06
Max.	13.04	38.96	8.15	82.08	123.74	20.58
Mean	9.50	32.03	4.43	62.91	108.87	14.84
Sd	2.11	3.81	1.36	10.46	11.84	4.55

Fig. 1. Relative abundance of Ba in F₁ (acid soluble), F₂ (reducible), F₃ (oxidizable), and F₄ (residual) of the soil samples.

($r = 0.897$). Such findings indicated that Ba could be bound by sulfur and then precipitated. Barium is not mobile as much during the decomposition since it precipitates easily in the sulfate and carbonate forms and is also strongly adsorbed by clay minerals (27). There were significant negative correlations between the soil CaCO_3 content and the F_3 fraction of Ba ($p < 0.05$).

Relationship Between Ba Concentrations in Different Fractions in Soil and Cherry Leaf Uptake

In this study, hierarchical cluster analysis (HCA) was performed, and a dendrogram was generated to assess the relationship between Ba concentrations in different fractions

in the soil samples and the leaf Ba contents (Figure 2).

The cluster analysis revealed a relationship between the leaf Ba content and the F_1 fraction (Figure 2). This indicated that plants were able to get trace metals initially at the F_1 fraction. Present findings revealed that the relationship between soil-extracted Ba concentrations and leaf Ba content could be used to assess the bioavailability of trace metals. It was observed that Ba in the soil matrix could easily intrude into the food chain, especially in the F_1 fraction and then in the F_2 and F_3 fractions. The relationship between the more mobile and easily available F_1 fraction and plant uptakes may reveal

significant information about the toxicity of this metal.

CONCLUSION

The findings of the present study showed that the total Ba concentrations in the soil of cherry orchards were not reliable indicators of plant uptake. Present findings focusing on soil and leaf samples taken from cherry orchards could be summarized as:

(i) Soil Ba concentrations were within the general ranges specified for soils. The sequential extraction procedure revealed that Ba was mostly present in the residual fraction (F_4) and secondly in the reducible fraction (F_2). Sequential extractions also revealed that Ba had 42% mobile phases.

(ii) Based on the present findings, it was observed that Ba has already reached the soils of cherry orchards, accumulated there, and could easily intrude the water systems and plant production system based on mobile quantities. Therefore, it is recommended that Ba should be monitored in agricultural fields for environmental protection and to safeguard human nutrition. Further research is recommended for the study of Ba concentrations in fruits.

TABLE IV
Pearson's Correlation Matrix (r) Between Ba Concentrations in Different Fractions of Soils and Selected Soil Characteristics (N=15)

Ba Fractions	Soil Properties		
	pH	CaCO_3 (%)	OM (%)
Acid-soluble (F_1)	-0.899*	-0.411	0.570*
Reducible (F_2)	-0.013	-0.342	0.701*
Oxidizable (F_3)	-0.335	-0.533*	0.897*
Residual (F_4)	0.331	0.172	-0.291
Total (ΣF)	0.098	-0.093	0.173

*: At 95% confidence level ($p < 0.05$).

Fig. 2. Dendrograms resulting from the hierarchical cluster analysis (HCA) in each fraction of Ba in the soil samples and uptake by cherry leaves.

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