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A GEOCHEMICAL INVESTIGATION OF SOILS, APPLES AND LEAVES IN AGIA AREA, CENTRAL GREECE

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Abstract

Forty two soil, apple and leaf samples from Agia area, central Greece, were collected and analyzed for their content in 7 major elements (Ca, Fe, K, Mg, Na, P and S). The average concentration of the determined elements follows the order: concentration in soils > concentration in leaves > concentration in apples. Elements, such as Fe that is found enriched in the soils of the study area, due to local geology, is not correlated with its concentrations in apples and leaves, possibly because of its association with resistant minerals. On the other hand, the relationship of some elements (i.e., K, P, S) that are constituents of the agrochemicals applied in the area, indicate that they are more readily available by the trees, either because they are associated with less resistant (clay) minerals, or because they derive through the application of agrochemical products (i.e., phosphate fertilisers, fungicides etc.).
Keywords: *mobility of chemical element, environment, fertilizer, agrochemical.*

Περίληψη

Σαράντα δύο δείγματα εδάφους, μήλων και φύλλων από την περιοχή της Αγιάς στην κεντρική Ελλάδα (Λάρισα) συλλεχτήκαν και αναλύθηκαν για το περιεχόμενο τους σε 7 κύρια στοιχεία (Ca, Fe, K, Mg, Na, P και S). Η επεξεργασία των δεδομένων έδειξε ότι η μέση συγκέντρωση των αναλυθέντων στοιχείων είναι μεγαλύτερη στα εδάφη, μετά στα φύλλα και τέλος, στα μήλα. Η στατιστική ανάλυση δεν έδειξε να υπάρχει κάποιος συσχετισμός μεταξύ των συγκεντρώσεων στοιχείων (π.χ., Fe) που είναι εμπλουτισμένα στα εδάφη, λόγω της τοπικής γεωλογίας και τη συγκέντρωση τους στα μήλα και φύλλα, πιθανότατα λόγω της σύνδεσης αυτών με ανθεκτικά ορυκτά. Αντίθετα, οι σχέσεις μεταξύ ορισμένων στοιχείων όπως K, P και S, τα οποία βρίσκονται στις διάφορες αγροχημικές ουσίες που εφαρμόζονται στην περιοχή δείχνουν πως μπορούν να απορροφηθούν πιο εύκολα από τα δέντρα, είτε γιατί σχετίζονται με λιγότερο ανθεκτικά (αργιλικά) ορυκτά, είτε γιατί προέρχονται από τη χρήση διάφορων αγροχημικών προϊόντων (π.χ., φωσφορικά λιπάσματα, ζιζανιοκτόνα κλπ.).
Λέξεις κλειδιά: *κινητικότητα χημικών στοιχείων, περιβάλλον, λίπασμα, αγροχημική ουσία.*

1. Introduction

Trees and plants and, consequently, their fruits and leaves, may contain and/or accumulate chemical elements depending on several attributes (i.e., soil chemical content, area of cultivation, method of cultivation, individual fruit/plant properties and others), contributing this way to the daily need of humans in such nutrients (Wagner, 1993; Bobrowska-Grzesik and Jakobik-Kolon 2008; Skordas *et al.*, 2013). Some of these elements are called "*macronutrients*" (i.e., Ca, Fe, K, P etc.). They are considered as essential, or at least more essential than others, to the life cycles of organisms and are absorbed by them in significant amounts (Kabata-Pendias and Pendias, 2001).

At the same time, soils enriched in chemical elements, either through natural factors or through man-made procedures could be considered as an additional aspect to the problem as they could pass through it to fruits consumed by humans. The content of chemical elements in soils is highly affected and differentiated by the nature of parent materials (Kelepertsis *et al.*, 2001; Skordas and Kelepertsis, 2005; Papastergios *et al.*, 2009, 2010, 2011; Petrotou *et al.*, 2010, 2012; Skordas *et al.*, 2013). The latter controls, along with other factors (i.e., soil pH, Eh, absorptive power of soil constituents etc.) the level of the element availability and their uptake from plants and animals in sufficient and, in some cases, even toxic levels (Alloway *et al.*, 1988; Alloway, 1995; Hesterberg, 1998; Kabata-Pendias and Pendias, 2001; Newman and Unger, 2003).

The aim of the present research was to study the concentrations of seven major elements (Ca, Fe, K, Mg, Na, P, S) as well as, investigate the relationship between the content of these elements in soils, apples and leaves from Agia area, Thessaly, central Greece. This research advances the knowledge offered by a previous work (Skordas *et al.*, 2013) as it examines the interrelationships between three means (soils, apples and leaves), contrary to the previous one which offered data and analysis only for two (soils and apples).

2. Materials and Methods

2.1. Study area - Geological setting

The study area is located in the eastern part of the Regional Unit of Larissa, central Greece (Fig. 1). It is a region with a plain relief that is surrounded by low hills in the eastern and southern part. The large plain of Larissa lies to the west of the studied area. Most part of the surface is covered by apple tree orchards, while a large portion of the mountainous area and the hills are covered by mountainous forest.

The area consists of metamorphic rocks, belonging to the Pelagonian zone. The main geologic formations are (Skordas and Kelepertsis, 2005; Skordas *et al.*, 2010, 2013): Quaternary sediments, Neogene sediments, marbles, metamorphic rocks (i.e., gneisses-schists, amphibolite schists, amphibolites) and ophiolites.

Because of the extensive cultivation several agricultural products such as fertilizers and agrochemicals (i.e., pesticides, fungicides and insecticides) are applied. Some of the most common substances used are chlorpyrifos, diflubenzuron, dithianon, flufenoxuron, myclobutanil, paraffin oil, phosmet, pyriproxyfen, thiacloprid, copper oxychloride, sulphur etc. These substances are applied to the orchards most commonly between March and September, but sometimes application could take place all year long. Fertilizer application usually happens during January, while the fruits are harvested around September.

2.2. Sampling, sample preparation and methods

A total of 42 samples from each sample type (soil, apple, leaf) were collected covering an area of 65 km^2, approximately. During the sampling procedure the initial regular sampling grid of 500x500 m was impossible to follow accurately, because of the cultivated and, in some parts, mountainous terrain. However, care was taken to preserve a uniform distribution of sampling sites over the study area (Fig. 1). In the case of the apples and leaves, the samples were collected from the apple tree that was nearest to the location of the soil sample. A more detailed description of the sampling and treatment procedure is described in Skordas *et al.* (2013). Soil samples were analyzed for their elemental content by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), while for the apples and leaves Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) was used.

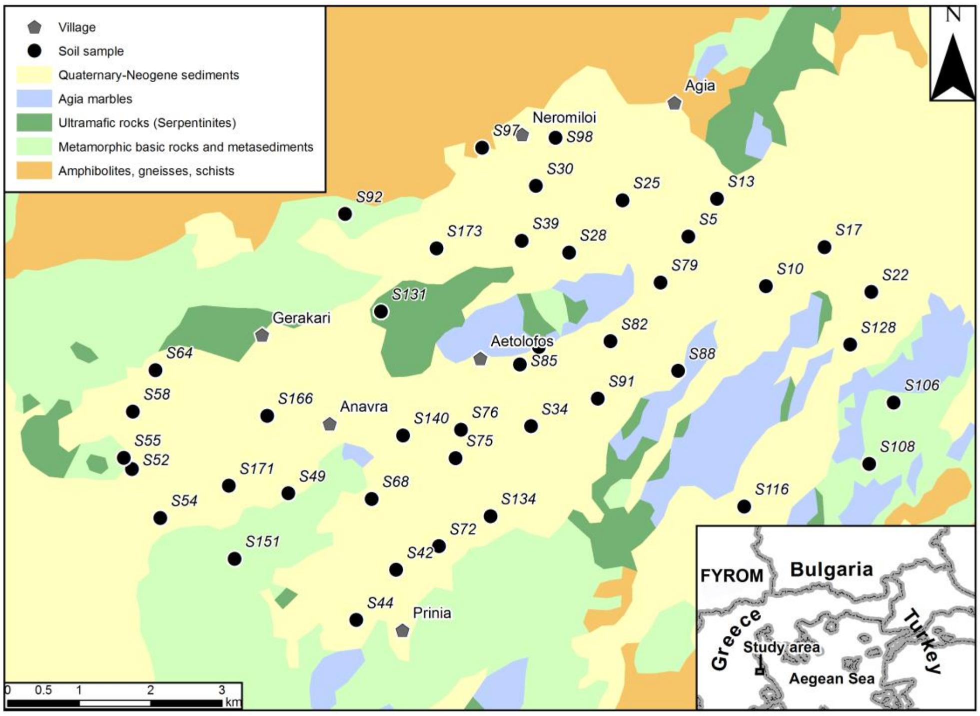

Figure 1 - Simplified geological map of the study area and sample locations (modified after Skordas *et al.*, 2013).

3. Results and Discussion

Descriptive statistics regarding the elements determined in the present study are given in Table 1. The most abundant element in soil is Fe, followed by Ca, Mg, Na, K and P. The rather elevated concentrations of Fe and Mg, were expected, as in the study area ophiolitic (ultramafic) rocks, which contain the above mentioned elements in noteworthy amounts, are present (Skordas and Kelepertsis, 2005; Petrotou *et al.*, 2010, 2012; Skordas *et al.*, 2010, 2013). A study (Kelepertzis, 2014) regarding agrcultural soils in Argolida, Greece, has reported slightly different average concentrations for Fe, P and K (27100 mg kg^{-1}, 3000 mg kg^{-1} and 900 mg kg^{-1}, respectively).

In apples, the most abundant element is K, followed by P, Mg, Ca, S, Na and Fe, while in leaves Ca is the element with the largest average concentration, followed by K, Mg, P, S, Fe and Na.

3.1. Overall assessment

For the majority of the determined elements their average concentrations follow the order: *concentration in soils* > *concentration in leaves* > *concentration in apples* (Table 1, Fig. 2). The same behaviour is demonstrated by the rest of the calculated statistic parameters, as well (Table 1). However, P is an exception to this behaviour. Its average concentration in soils (1119 mg kg^{-1}) is about the same as in apples (881.7 mg kg^{-1}) and lower than in leaves (2073 mg kg^{-1}). This could be a result of the excessive application of phosphoric fertilizers or/and organophosphate agrochemicals such as chlorpyrifos ($C_9H_{11}C_{13}NO_3PS$) and phosmet ($C_{11}H_{12}NO_4PS_2$). It also can be deducted that, probably, the determined elements accumulate more in leaves than in fruits (apples).

Table 1 - Descriptive statistics regarding the elements determined in soils, apples and leaves.

(mg kg^{-1})	Soil	Leaf	Apple	Soil	Leaf	Apple
Element		**Ca**			**Fe**	
median	25250	16350	400.0	45300	195.0	15.0
average	25390	16860	390.5	46486	228.1	28.3
geomean	23813	16593	383.5	45916	208.4	19.4
minimum	11600	11400	300.0	31200	110.0	10.0
maximum	70400	25700	600.0	65200	690.0	150.0
std deviation	10117	3078	75.9	7364	112.9	31.5
Element		**K**			**Mg**	
median	13950	11800	9550	20250	4935	480.0
average	13543	11964	9676	20088	5052	474.8
geomean	13303	11713	9545	19557	4976	470.8
minimum	8300	6600	6000	9900	3590	360.0
maximum	17300	16500	14700	32700	7440	610.0
std deviation	2448	2409	1632	4633	907.3	62.3
Element		**Na**			**P**	
median	15100	80.0	40.0	975.0	2040	865.0
average	14924	89.8	42.1	1119	2073	881.7
geomean	14629	83.8	40.5	1019	2043	869.4
minimum	8800	50.0	30.0	430.0	1410	590.0
maximum	23900	250.0	90.0	4290	3440	1190
std deviation	3040	37.9	13.2	619.4	378.5	148.3
Element		**S**				
median		1900	300.0			
average		1874	302.4			
geomean		1862	245.3			
minimum		1500	50.0			
maximum		2400	800.0			
std deviation		213.1	181.1			

Phosphate fertilizers are considered as an important source of heavy metals entering agricultural soils (Nicholson *et al.*, 2003; Rodriguez Martin *et al.*, 2006). Other elements (heavy metals) are also present in varying amounts in other inorganic fertilizers (i.e., nitrogen, potash) and in liming materials (Nicholson *et al.*, 2003; Rodriguez Martin *et al.*, 2006). The excessive application of such substances could lead to elevated concentrations in agricultural products cultivated over these soils (Otte *et al.*, 1993; Dudka *et al.*, 1994; Rodriguez Martin *et al.*, 2006; Skordas *et al.*, 2013). Hence, the elevated values of such elements in the apples of the present study could derive from the excessive amounts of fertilizers and agrochemicals applied to the local crops.

3.2. Elemental relationships between the sampled means

Additionally, correlation analysis was carried out to determine the nature of the relationships between the investigated elements. Because the data of the present research were not normally distributed the estimation of Spearman's rank correlation coefficient (also known as Spearman's *rho*) was selected (non-parametric statistics). Unless otherwise stated, correlations were considered significant at $p < 0.01$.

In soils, elements that are significantly correlated are Na and Ca (r: 0.52), Fe and Mg (r: 0.40) and P and Ca (r: 0.52) (Table 2). In apples (Table 3), the latter correlation applies for K and Mg (r: 0.61) and K and P (r: 0.44), while a correlation (at the 0.05 level) is also displayed by Ca and Mg (r: 0.32) and Mg and P (r: 0.36). Finally, in leaves (Table 4), the only correlation present is between K and Mg (r: -0.36), which, is negative ($p < 0.05$).

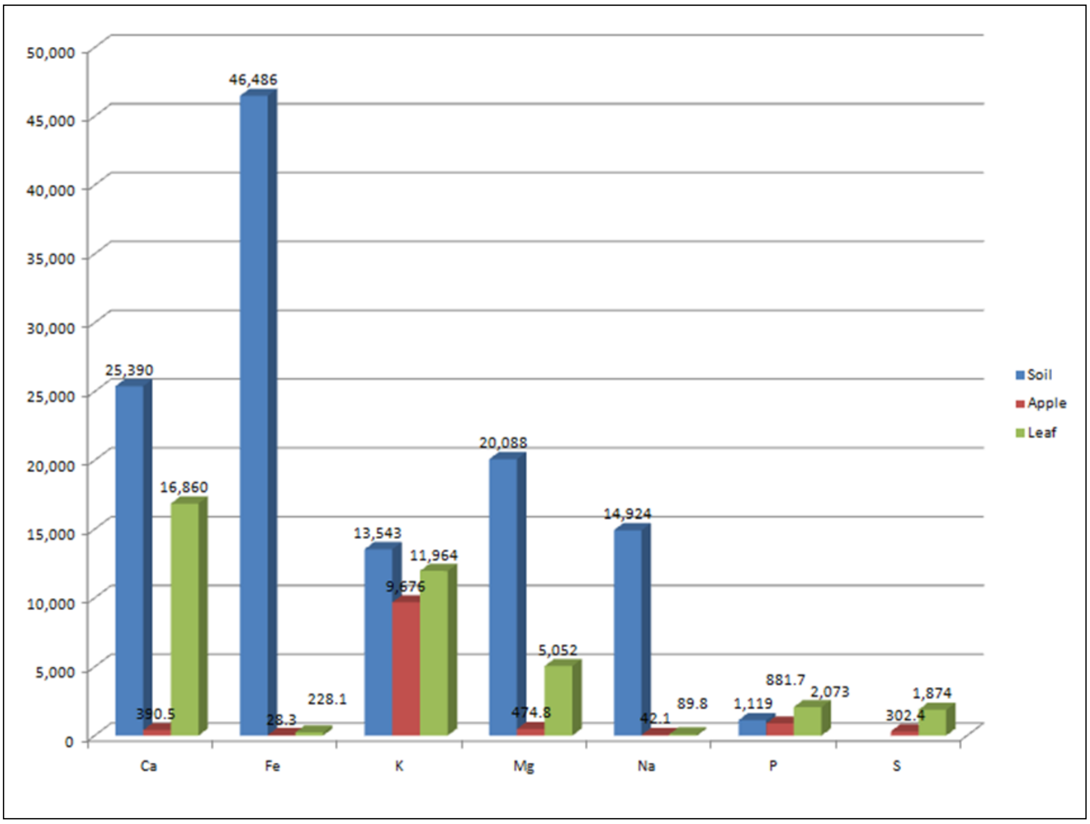

Figure 2 - Graphical representation of the average elemental concentrations determined in soils, apples and leaves.

Table 2 - Spearman's rank correlation coefficient (Spearman's *rho*) for the determined elements in soils (S) and apples (A).

	Ca_S	Ca_A	Fe_S	Fe_A	K_S	K_A	Mg_S	Mg_A	Na_S	Na_A	P_S	P_A
Ca_S	1											
Ca_A	-.242	1										
Fe_S	.111	.137	1									
Fe_A	-.004	-.231	-.134	1								
K_S	-.175	.112	-.133	-.104	1							
K_A	.170	-.021	.119	-.064	-.054	1						
Mg_S	.120	-.049	.401**	.070	.174	.012	1					
Mg_A	-.145	.316*	-.002	-.105	-.206	.612**	-.164	1				
Na_S	.520**	-.201	.010	.363*	-.198	.183	-.045	-.103	1			
Na_A	-.057	-.011	-.270	-.050	-.129	.051	-.159	.146	-.025	1		
P_S	.525**	-.049	.110	.027	-.078	.229	.099	.089	.268	-.154	1	
P_A	.162	-.034	-.203	.108	-.226	.441**	-.154	.356*	.370*	.159	.002	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 3 - Spearman's rank correlation coefficient (Spearman's *rho*) for the determined elements in soils (S) and leaves (L).

	Ca_S	Ca_L	Fe_S	Fe_L	K_S	K_L	Mg_S	Mg_L	Na_S	Na_L	P_S	P_L
Ca_S	1											
Ca_L	.209	1										
Fe_S	.111	.006	1									
Fe_L	.011	-.139	-.168	1								
K_S	-.175	.073	-.133	.211	1							
K_L	-.003	-.256	-.071	-.001	.059	1						
Mg_S	.120	.167	.401**	.015	.174	-.006	1					
Mg_L	.310*	.226	-.126	.171	-.224	-.362*	.010	1				
Na_S	.520**	.008	.010	.035	-.198	-.033	-.045	-.061	1			
Na_L	.248	.097	.050	.225	-.058	-.299	-.009	.232	.249	1		
P_S	.525**	.043	.110	.159	-.078	.156	.099	-.004	.268	.016	1	
P_L	-.015	-.120	-.229	.015	.013	.191	-.038	-.129	.127	.025	-.316*	1

Table 4 - Spearman's rank correlation coefficient (Spearman's rho) for the determined elements in leaves (L) and apples (A).

	Ca_L	Ca_A	Fe_L	Fe_A	K_L	K_A	Mg_L	Mg_A	Na_L	Na_A	P_L	P_A	S_L	S_A
Ca_L	1													
Ca_A	-.022	1												
Fe_L	-.139	-.175	1											
Fe_A	.161	-.231	.350*	1										
K_L	-.256	-.146	-.001	-.243	1									
K_A	-.057	-.021	.145	-.064	.517**	1								
Mg_L	.226	-.052	.171	.162	-.362*	-.110	1							
Mg_A	-.265	.316*	.241	-.105	.261	.612**	-.083	1						
Na_L	.097	.027	.225	.165	-.299	.005	.232	.001	1					
Na_A	-.041	-.011	-.068	-.050	-.007	.051	.160	.146	.369*	1				
P_L	-.120	.025	.015	.120	.191	-.216	-.129	-.158	.025	.208	1			
P_A	-.107	-.034	.226	.108	.152	.441**	.066	.356*	.066	.159	.366*	1		
S_L	-.196	-.026	.237	-.198	.300	.097	-.416**	.257	-.132	.161	.072	-.222	1	
S_A	-.049	-.108	.290	.143	.264	.194	-.069	.172	-.325*	-.360*	.009	.109	.159	1

Nevertheless, when examining the elemental relationships amongst the different sampling in general, no significant correlation was found among the concentrations that the studied elements have in soils and apples, and in soils and leaves (Tables 2 and 3), indicating that for the studied elements their concentrations in apples and leaves is not strongly influenced by their concentration in soils. One would expect that, since these trees grow on soil enriched in Fe its elevated concentrations would be directly associated with their geogenic origin. Possibly, because Fe is found in resistant minerals is not readily available (Megremi, 2010; Petrotou *et al.*, 2010).

However, strong correlations between the concentrations of K and Mg, as well of Fe, Na and S (at $p < 0.05$), in apples and leaves has been noted (Table 4). Elements (i.e., Na, Ca) that are associated with clay minerals, such as montmorillonite, could be more easily extracted from the trees and accumulate in different parts, thus, the existing correlation between this elements in apples and leaves. Another way for this elements to accumulate in apples and leaves could be through the application of the various agrochemical substances applied, as the strong correlation between P and Na implies (Table 4).

4. Conclusions

The treatment of the data presented in this research has shown that the average concentration of the determined elements follows the order: *concentration in soils > concentration in leaves > concentration in apples*. Elements, such as Fe that is found enriched in the soils of the study area is not correlated with its concentrations in apples and leaves, possibly due to its association with resistant minerals. On the other hand, the relationship of some elements (i.e., K, P, S) that are constituents of the agrochemicals applied in the area, indicate that they are more readily available by the trees, either because they are associated with less resistant (clay) minerals, or because they derive through the application of agrochemical products (i.e., phosphate fertilisers, fungicides etc.).

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