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Seasonal change of the mineral concentrations of gall oak (*Quercus infectoria*) and Christ's-thorn (*Paliurus spina-christi*)

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Abstract. Gall oak and Christ's-thorn are common in the Mediterranean flora of Turkey and significant forage source for goats in spring, summer and fall. Both species are consumed preferably by the goats. Therefore, to obtain information about the feeding values of these species and reveal cause of the goats preferred primarily these species were aimed in this study by determining the change of nutrient and non-nutrient minerals in these species. In the samples macro and micro elements were determined. Results were analyzed statistically by repeated experimental design. Generally, seasonal variation of minerals of both shrubs was similar. While N, P, K, S, Cu and Zn decreased regularly from spring to fall, Ca, Mn and Na increased. Mg did not alter significantly. In gall oak, B increased from spring to fall and decreased in Christ's-thorn from spring to summer. Although Zn amount of gall oak had non-significant change seasonally, it was high for Christ's-thorn in spring but low in the other seasons. The shrubs contained sufficient macro and micro nutrients, except for S, Cu and Zn, to supply the needs of the goats in every season.

Keywords. Gall oak – Christ's thorn – Macronutrient – Micronutrient.

Variations saisonnières des concentrations en minéraux chez Quercus infectoria et Paliurus spina-christi

Résumé. Quercus infectoria *et* Paliurus spina-christi *sont des espèces courantes de la flore méditerranéenne de Turquie et constituent une importante source de fourrage pour les caprins au printemps, en été et en automne. Ces deux espèces sont consommées de préférence aux autres par les caprins. Ainsi, pour obtenir de l'information sur la valeur alimentaire de ces espèces et révéler pourquoi les caprins les préfèrent, nous avons cherché dans cette étude à déterminer les modifications des minéraux nutritionnels et non nutritionnels chez ces espèces. Les macro et micro-éléments ont été dosés dans les échantillons. Les résultats ont été analysés statistiquement par dispositifs expérimentaux répétés. Généralement, la variation saisonnière des minéraux était semblable chez les deux arbustes. Tandis que N, P, K, S, Cu et Zn baissaient régulièrement du printemps à l'automne, Ca, Mn et Na augmentaient. La valeur de Mg n'a pas été modifiée significativement. Chez* Quercus infectoria*, la valeur de B a augmenté du printemps à l'automne tandis qu'elle a baissé chez* Paliurus spina-christi *du printemps à l'été. Bien que la teneur en Zn chez* Quercus infectoria *n'ait pas subi de variations significatives au cours des saisons, elle était élevée chez* Paliurus spina-christi *au printemps mais faible lors des autres saisons. Les buissons contenaient suffisamment de macro et micro-nutriments, sauf pour S, Cu et Zn, afin de couvrir les besoins des caprins pendant toutes les saisons.*

Mots-clés. Quercus infectoria – Paliurus spina-christi – *Macronutriment – Micronutriment.*

I – Introduction

Shrubs are considered as natural forage sites for goats especially in maquis lands with dry summers. Therefore, goats are mostly raised over these sites (Rogosic *et al*., 2006). Grazing researches carried out over shrubby rangelands of Mediterranean Region revealed that shrubs constituted more than 60% of goat forage (Papachristou *et al*., 2005). Although shrubs generally

have low forage quality and have secondary metabolites decreasing the succulence (Bartolomé *et al.*, 1998), leaves and fresh shoots have higher protein rates and lower fiber contents than grasses (Bartolomé *et al.*, 1998). Deciduous shrubs like gall oak and Christ's-thorn have higher nutritional values than the other shrubs and herbaceous species (Temel and Tan, 2011). Nutrients usually constitute the structural members of significant compounds in plants, play a role in enzyme activity and form complexes with organic molecules (Whitehead, 2000). However, these nutrients do not present at constant rates in plants. Most of them (N, P, K, S, Cu) significantly decrease with the maturation. As leaves senescence, nutrient losses are observed through remobilization and washout by precipitations (Whitehead, 2000).

Shrubs cover about 8.5 million hectare land area in Turkey (Anon., 1978) and significant part of these lands is located in Mediterranean zone. On the other hand, goats constitute 15.3% (6.3 million) of total 41.4 million livestock assets of Turkey (Anon, 2010). The research activities on shrubs of Marmara Region are not sufficient. Therefore in this study, year-around variation in macronutrient, micronutrient contents of gall oak and Christ's-thorn were observed. In this way, the significance of shrubs for goats was put forward.

II – Materials and methods

The research was carried out over shrubby rangelands located within Ağaköy, 85 km from Çanakkale Province between the dates October 2006 and November 2007. Monthly average temperatures (15.1°C) during the research period were higher than the long-term averages (13.9°C).Winter, spring and summer precipitations were lower than long-term averages. Soils of research site are sandy-loam, neutral, unsaline with high organic material content, sufficient available P and sparse K content. Exchangeable Ca, Mg, K, Na and CEC were 13.42, 2.64, 0.17, 0.07 and 16.42 meq/100 g, respectively.

In this research, gall oak (*Quercus infectoria* Oliv.) and Christ's-thorn (*Paliurus spina-christi* Miller) were used as the plant material. During the research period, plant samples were taken from the shrubs in the middle of each month. Leafy young shoots (twigs), grazable by animals, were cut and collected. Ten samples were taken from each species in each sampling. Since the investigated shrubs are deciduous shrubs, samples were not taken during the period from defoliation in fall to leaf-turn in spring. Samples were placed into cloth bags, they were dried and grinded. Macro and micronutrients were analyzed in these samples. Total nitrogen was determined by Kjeldahl method and other elements (P, K, Ca, Mg, S,Fe, Mn, Cu, B, Na, Zn) were determined by ICP-AES. Research was established using the repeated measurement design and data was statistically analyzed by SPSS statistical software. LSD Multiple Comparing Test was used to compare the averages.

III – Results and discussion

While the seasonal variations in Mg and Zn were found to be insignificant, variation of other elements were found to be significant. The highest N, P, K, S and Cu contents of gall oak were observed in spring and the values decreased in summer and fall. On the other hand, Ca, Fe, Mn, B, Na contents were at the lowest levels in spring and the values were generally higher in other seasons. Seasonal variations in Cu, B, Se content of Christ's-thorn were found to be significant. While N, P, K, S, Zn were higher during the plant growth in spring than the other seasons, Ca, Mn and Na increased in fall. Mg, Fe increased both in spring and fall seasons. Mineral content of Christ's-thorn generally decreased in summer (Table 1).

There are close relationships between N, P, K and S concentrations and physiological activities of plants. Nitrogenous compounds act as biocatalyst enzymes in plants, P plays a role in energy systems (ATP) and exists in structure of nucleic acids together with nitrogen, K regulates the osmotic potentials of the cells and S exists in structures of proteins (Kacar and Katkat, 2007).

Therefore, most of these elements exist within cell protoplasm (Spears, 1994). Although young cells in plants have high protoplasm rates, the value decreases and rate of cell wall increases as the plant maturates and dries out. Therefore, the highest N, P, K and S ratios in gall oak and Christ's-thorn were observed in spring and the lowest levels were observed in summer and fall. Similarly, Mountousis *et al.* (2008) observed the highest N ratio of the shrubs in spring and decreased values with plant maturation. Also, El Aich (1991) indicated decreasing P concentrations with maturation and Fleming (1973) reported unchanged Ca content and significantly decreased P and K ratios.While Ca contents of shrubs decreased distinctively in spring, the value increased in other seasons. Ca usually exists in hard tissues of the plants (Spears, 1994). Current results were mostly due to high protoplasmic compound levels and low wall compound levels at the beginning of growth.Variation in Mg content of gall oak was found to be significant and the values for Christ's-thorn increased significantly in spring and fall. Although most of Mg exists in protoplasm (Spears, 1994), a regular seasonal variation was not observed in plants. Researchers reported different results with regard to variation of Mg in plants. For instance, Ramírez-Orduña *et al.* (2005) reported insignificant seasonal variations in Mg contents of shrubs and Ramírez *et al.* (2001) determinate significant variations in Mg contents.

Table 1. Mineral concentrations of gall oak and Christ's-thorn

Season	**Gall oak**					
	N	**P**	**K**	**Ca**	**Mg**	**S**
Spring	23.33±4.8a	3.24±1.1a	9.65±2.7a	5.32±2.2c	3.44±0.4	1.34±0.3a
Summer	15.97±2.2b	2.12±0.2b	6.15±0.4b	12.46±2.6b	3.33±0.3	0.94±0.1b
Fall	14.68±3.9b	2.18±0.3b	4.40±1.3c	16.16±1.8a	3.46±0.6	0.93±0.1b
Mean	*17.99*	*2.51*	*6.73*	*11.31*	*3.41*	*1.07*
Significance	*0.000*	*0.002*	*0.000*	*0.000*	*0.755*	*0.000*
	Fe	**Mn**	**Cu**	**B**	**Na**	**Zn**
Spring	130.4±29.2b	590.0±156.6b	10.24±3.4a	22.5±2.7c	730.7±109.4b	27.7±6.8
Summer	277.0±68.7a	1234.8±259.0a	7.10±0.8b	46.1±10.5b	773.3±65.8b	25.0±4.2
Fall	309.4±66.6a	1342.8±220.5a	6.89±1.0b	62.0±13.6a	1201.9±281.5a	26.6±3.7
Mean	*238.9*	*1055.9*	*8.08*	*43.6*	*902.0*	*26.4*
Significance	*0.000*	*0.000*	*0.002*	*0.000*	*0.000*	*0.402*
	Christ's-thorn					
	N	**P**	**K**	**Ca**	**Mg**	**S**
Spring	25.30±8.6a	4.73±0.9a	16.87±1.3a	10.40±2.0c	3.08±0.8a	1.81±0.2a
Summer	19.36±4.9b	2.18±0.4b	13.65±1.9b	16.07±4.7b	2.36±0.4b	0.91±0.01c
Fall	14.14±2.1b	1.78±0.2b	10.05±3.2c	23.25±6.2a	2.85±0.9a	1.04±.004b
Mean	*19.60*	*2.90*	*13.52*	*16.57*	*2.76*	*1.25*
Significance	*0.003*	*0.000*	*0.000*	*0.000*	*0.001*	*0.000*
	Fe	**Mn**	**Cu**	**B**	**Na**	**Zn**
Spring	133.8±24.9a	627.3±127.4b	7.61±1.3	65.6±5.6	660.2±65.8b	40.4±9.7a
Summer	87.0±22.4b	592.0±319.7b	6.71±1.9	51.4±4.2	663.8±98.4b	24.8±3.9b
Fall	130.9±30.2a	961.0±355.5a	6.38±1.3	51.4±7.2	813.0±238.9a	23.7±4.3b
Mean	*117.2*	*726.8*	*6.90*	*56.1*	*712.3*	*29.6*
Significance	*0.000*	*0.000*	*0.080*	*0.060*	*0.003*	*0.000*

Higher Fe concentrations in gall oak were observed in summer and fall and higher ratios in Christ's-thorn were observed in spring and fall. Fe contents of plants are affected by soil conditions and changes in climate and growth seasons (Macpherson, 2000). Different results might be attributed to these issues. Fe is closely related to enzyme systems of the plants. It plays an activating role in biochemical processes like photosynthesis, respiration and N fixation (Kacar and Katkat, 2007). Therefore, higher Fe concentrations, were expected to be observed in spring, as it occurred in the case of Christ's-thorn. This expectation was also supported by Ramírez-Orduña *et al.* (2005). Mn contents of gall oak increased in summer and fall and the value of Christ's-thorn increased in fall. Most of Mn exists in cell wall of the plants (Spears, 1994). Therefore, higher rates are expected especially in summer and fall. On the other hand, insignificant seasonal changes in Mn contents were reported in the research carried out in Mexico (Ramírez-Orduña *et al.*, 2005). While higher Cu ratios of shrubs were observed in spring, the values decreased with maturation. Decrease in Cu content usually occurs with maturation, changes in climate and seasonal variations (Spears, 1994). Since Cu takes place into protein synthesis of plants, it generally exists intensively in physiologically active cells. Therefore, higher Cu contents are observed in spring (Ramírez *et al.*, 2005). Boron concentrations of gall oak increased from spring to fall and significant variations were not observed in Christ's-thorn. B plays a role in sugar synthesis and transport, in synthesis of nucleic acids and plant hormones (Kabata-Pendias, 2001) and in cell membrane processes (Kacar and Katkat, 2007). Even being insignificant, these roles may explain the high B ratios of Christ's-thorn in spring. Since B is also bound to cell wall with weaker bonds than Ca (Kacar and Katkat, 2007), B content of gall oak might increase during the maturation. Na contents of shrubs increased in fall. Na contents of plants vary based on plant species, growth stages, climate and soil conditions. Higher Na rates are observed especially in dry sites and dry years (Ramírez-Orduña *et al.*, 2005). In current study, lower precipitations in fall and winter than long-term averages might be effective to have such findings. Zn content of Christ's-thorn increased in spring and decreased in summer and fall. The variation in gall oak was found to be insignificant. Zn constitutes especially the basic structure of some enzyme systems participating into protein synthesis (Kacar and Katkat, 2007). Increasing Zn contents of Christ's-thorn in spring may be tied to high protein rates in plants at the beginning of growth (in spring).

IV – Conclusions

Evaluations made by taking the goats into consideration revealed that only S, Cu and Zn were found to be insufficient for goats during the growth seasons of both shrubs.

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