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CONTENTS

ORIGINAL PAPERS

ANTIBACTERIAL ACTIVITY OF Ag-MODIFIED GRAPHENE OXIDE COMPOSITES 1494
Aijun Gu and Wei Chen

PRODUCTION OF ACTIVATED CARBON FROM RICE HUSK TO SUPPORT Zn^{2+} IONS 1499
Esra Altıntıg, Isa Acar, Huseyin Altundag and Omer Ozyıldırım

RELATIONSHIPS BETWEEN SITE INDICES AND ECOLOGICAL FACTORS FOR BLACK ALDER STANDS IN THE TURKISH EASTERN BLACK SEA REGION 1507
Murat Yılmaz, Ayhan Usta and İrfan Öztürk

APPLICATION OF MULITIVARIATE STATISTICAL METHODS FOR ANALYSIS OF PHYSICAL AND CHEMICAL FACTORS IN RESERVOIR WITH SEPARATED PRE-DAM ZONE ON THE BASIS OF THE EXAMPLE OF JEZIORO KOWALSKIE 1516
Mariusz Sojka, Jolanta Kanclerz, Tomasz Dysarz and Joanna Wicher-Dysarz

INVESTIGATION OF THE EFFECT OF BLENDING RATIO AND TEMPERATURE ON THE KINEMATIC VISCOSITY AND SPECIFIC GRAVITY OF WASTE COOKING OIL BIODIESEL 1523
Tanzer Eryilmaz and Murat Kadir Yesilyurt

EMISSION REDUCTION EFFECTS OF BIOGAS MICRO-DIGESTERS: A CASE STUDY OF RURAL HOUSEHOLDS IN KAIXIAN, CHINA 1530
Donghai Yuan, Jiayuan Wang, Xueju Huang, Xufeng Mao, Zhiqiang Hong, Jinggang Wang, Yuan Cao and Junqi Li

NITRATE CONCENTRATION CHANGES IN A RIVER AND ITS RESERVOIR WITHIN AN AGRICULTURALLY-INFLUENCED WATERSHED: THE RIVER LEDAVA (SE AUSTRIA AND NE SLOVENIA) CASE STUDY 1537
Polona Ojsteršek Zorčič, Matjaž Mikoš, Katarina Košmelj and Marina Pintar

HYDROTHERMAL SYNTHESIS AND VISIBLE-LIGHT-DRIVEN PHOTODEGRADATION OF ANTIBIOTICS OF BI_2WO_6 NANOSTRUCTURES 1549
Xinying Li, Liping Wang, Weidong Shi, Gehong Zhang, Ao Ren and Chengjie Song

NITROGEN AND CARBON CONCENTRATIONS IN THE SAMPLES OF SOIL, SEDIMENT AND *PHRAGMITES AUSTRALIS* (COMMON REED) FROM KÜÇÜKÇEKMECE LAGOON AREA (ISTANBUL, TURKEY) 1558
Istvan Csatari, Gülriz Baycu, Ender Makineci, Szilard Szabo, Doganay Tolunay and Gyula Lakatos

ADSORPTION–CATALYSIS OF DYE USING MODIFIED BENTONITE 1568
Yizhong Chen and Chunyang Jiang

THE NUTRITIONAL CONDITIONS AND SOME HEAVY METAL CONTENTS OF THE VINEYARDS IN A SEMI-ARID AREA 1573
Bulent Yagmur, Senay Aydın, Harun Coban and Halis Simsek

EXTRACTION OF PAPAIN BY AN IONIC LIQUID-BASED AQUEOUS TWO-PHASE SYSTEM 1579
Jingyu Pang, Haiyan Ji, Jianjun Liu, Yanhong Chao, Lining He, Changri Han, Wenshuai Zhu and Huaming Li

DERIVATION OF PM10 LEVELS USING OBRA ON LANDSAT 5 TM IMAGES: A CASE STUDY IN IZMIR, TURKEY 1585
Emre Ozelkan, Muhittin Karaman, Suleiman Mostamandy, Z. Damla Uca Avci and Huseyin Toros

INDEX 1597

THE NUTRITIONAL CONDITIONS AND SOME HEAVY METAL CONTENTS OF THE VINEYARDS IN A SEMI-ARID AREA

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ABSTRACT

Turkey is one of the most important seedless raisin producers in the world market. Approximately, 82% of the seedless raisin has been produced in the western part of Turkey since the climate (semi-arid) of this region is very appropriate to grow seedless grape. More specifically, the Plain of Alasehir, located in the Gediz Basin in Aegean Region has been known its high quality seedless raisin production. About 25% of the seedless raisin of the entire Aegean Region is produced in the Plain of Alasehir. Therefore, the Plain of Alasehir region was selected to determine some heavy metal contents (Cd, Co, Cr, and Pb) and certain macro and micro element contents (N, P, K, Ca, Mg, Fe, Zn, Mn, and Cu) of the leaf samples obtained from the vineyards in the area. The plant samples from 13 vineyards were analyzed by collecting the samples across the first plant bunch during the veraison period. In terms of nutrition profile, N deficiency was detected in 15% of vineyards while P deficiency was determined in 38.5 % of the vineyards. Similarly, Fe deficiency was detected in the 30.8 % of the vineyards. The contents of Zn, Mn, Cu, K, Ca, and Mg were sufficient in all of the vineyards. Some heavy metal contents of the leaf samples were analyzed and it was found that there was no pollution for the Cd, Co, and Pb in all the vineyards. Cr pollution was not detected in 93.2% of the samples.

KEYWORDS: Vineyard, *Vitis vinifera* L., raisin, macro elements, micro elements, heavy metals.

1. INTRODUCTION

Fast growing big cities in Turkey face some environmental problems and extend their borders through rural areas where there is a high farming potential. Because of this overlap between industrialized big cities and rural areas, the pollution of soil, air and plants, which is also defined as environmental pollution, has started to appear in our agricultural areas. The pollution has negative impact on the quality and the quantity of the crop product. Usually, the pollutants are originated from industrial wastes or from the agricultural practices. Because of the disruption of ecological balance and natural biological development, chemical residues in agricultural products (such as chemical fertilizers, pesticides, and hormones) have begun to threaten human health. Heavy metals (Cd, Cr, Co, Pb, Ni, etc.) have been attracting researchers' interest for the last 20 years not only because they are the source of pollutants but also they are needed by the plants and animals for the physiological needs. While early studies were focusing on the analysis of the micro elements (such as Fe, Zn, Mn, and Cu) in soil, water and plants, the toxic metals (such as Cd, Cr, Pb, Ni, Ti, and Hg) were investigated later. All around the world, the goal of agricultural production is to obtain sustainable, satisfactory, high quality, and clean products.

Because of its semi-arid climate in the western part, Turkey is one of the top grape producing and exporting countries in the world in terms of having large vineyard areas and the wide range of grape varieties grown in the area. Especially, round seedless grapes are produced in Gediz basin, in the Aegean region, in Izmir, Denizli, Manisa, and in their surroundings (82 %). Total of 25 % of seedless raisin are produced and processed in the Plain of Alasehir, Manisa [1]. Similarly, 90 % of the vineyards that exist in the region are produced round seedless grapes (*Vitis vinifera* L.) [2]. In recent years, a large number of hormones, chemical drugs, and fertilizers have been used in the region in order to enlarge the size of the grapes so that the fruit quality could be improved. These practices raised some concerns in the export market. It is a well-accepted fact that quality grape production is impacted by not only the nutritional conditions, but also from many other factors [3,4]. The leaves have been known to be the best plant organ to reflect the nutritional status of plants, which is why analyses of the leaves have gained importance for examining the nutritional status of vineyards. Researchers have

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been studying the plant tissues to obtain the reference values for nutritional elements in different parts of leaves in various physiological periods [5-7]. In this context, the purpose of the present study was to determine some heavy metal contents, the level of pollution, some macro and micro element (N, P, K, CA, Mg, Fe, Mn, and Zn) contents and the nutritional conditions of vineyards in the plant (leaf) samples taken from the round seedless grape vineyards in the Plain of Alasehir in Gediz Valley.

2. MATERIAL AND METHODS

The locations of the vineyards where lamina samples were obtained are shown in Table 1. Samples for this study were collected as lamina during the veraison period from 13 different vineyards. Seedless grapes (*Vitis vinifera* L.) were grown in these vineyards, which were located in the Plain of Alasehir in the Aegean Region.

Samples were collected in August 2012 according to the method by Levy (1968) [5]. The total N in the leaf samples was measured using the modified Kjehldahl method, phosphorus (P) in wet digested samples with colorimetric, potassium (K) and calcium (Ca) with flame photometry, and magnesium (Mg), iron (Fe), zinc (Zn), manganese (Mn), and copper (Cu) were measured using Atomic Absorption Spectrometry (AAS) [8]. Boron (B) was measured using the colorimetric method with diantrimid method [9]. As for some heavy metals in leaf samples, they were determined after being converted into ash at 500-550 ^{OC} using AAS [10, 11].

3. RESULTS AND DISCUSSION

3.1 The contents of macro and micro elements of leaf samples

The average, minimum and maximum values of the macro elements (N, P, K, Ca, and Mg) and micro elements (Fe, Zn, Mn, Cu, and B) in the leaf samples are presented in Table 2 and Table 3.

Based on the results of the present study, the minimum, maximum, and average values of leaf samples belonging to the macro element contents are as follows; the total N was

TABLE 1 - The locations of the vineyards and name of the producers where leaf samples were obtained.

Vineyards (Samples)	*Vineyard location*	Name of the owner
1	*Kovalık*	Mehmet Ok
2	*Mezarlık*	Mustafa Onal
3	*Saglık ocagı*	Mehmet Aktas
4	*Kovalık*	Ahmet Yildirim
5	*Sellik*	Suleyman Ceylan
A	*Plain of Alasehir*	Cevdet Yavuz
B	*Plain of Alasehir*	Huseyin Basturk
C	*Plain of Alasehir*	Suleyman Basturk
D	*Plain of Alasehir*	Faruk Ozturk
E	*Plain of Alasehir*	Cengiz Ozturk
F	*Plain of Alasehir*	Izzet Cetin
G	*Plain of Alasehir*	Huseyin Topaloglu
H	*Plain of Alasehir*	Cengiz Sahin

TABLE 2 - Macro element contents of leaf samples collected from vineyard plantations.

Sample	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	K/Mg
1	2.18	0.15	1.58	1.66	0.62	2.55
2	2.25	0.17	1,.1	1.71	0.66	2.59
3	2.27	0.17	1.85	1.71	0.76	2.43
4	2.32	0.18	1.94	1.68	0.79	2.46
5	2.40	0.17	1.96	1.56	0.73	2.68
A	2.17	0.15	1.87	1.64	0.65	2.57
B	2.37	0.17	2.02	1.74	0.77	2.62
C	2.31	0.17	1.84	1.91	0.63	2.52
D	2.36	0.14	2.03	1.68	0.73	2.78
E	2.33	0.14	2.13	1.64	0.71	3,00
F	2.30	0.14	1.96	1.68	0.78	2.51
G	2.37	0.12	1.45	1.79	0.71	2.04
H	2.48	0.14	1.60	1.64	0.69	2.32
Average	2.32	0.15	1.85	1.70	0.71	2.51

between 2.18 and 2.48% (average 2.23%), P values were ranging from 0.12 to 0.17% (average 0.15%), K values were ranging from 1.45 to 2.13% (average 1.79%), Ca was between 1.56% and 1.91% (average 1.70%), and Mg values were ranging from 0.62 to 0.79% (average 0.71%) (Table 2). Conradie (1986) [6] suggested the reference (limit) values for the total N was ranging from 1.50 to 2.40% during the veraison period. Taking this reference value into consideration, total N in leaf samples were sufficient for enough nutrition. However, if we consider the reference values from Levy (1968) [5], Mills and Jones (1996) [8], and Robinson (1990) [12] that reported these values between 2.00% and 2.40%, 15% of vineyards (Vineyard Number 1 and A) had insufficient nutrition. Considering all the literature information, the vineyard soils from the same area are usually have sufficient N, which supported by our previous research studies [13,14]. Yener et al (2002) [14] found the values of total N, P, K, Ca, and Mg in the samples of leaf lamina during the veraison period as 2.03-2.87%, 0.12-0.36%, 0.60-1.10%, 1.46-3.18%, and 0.30-0.87%, respectively in their study which was carried out to determine the status of nutrient in the vineyards in the Kavaklidere in the Plain of Alasehir. Our results from this study also confirm these findings.

Chapman (1965) [15], Reuter and Robinson (1986) [16], and Mils and Jones (1996) [8] reported the phosphorus contents of leaf samples from lamina stage as 0.12-0.50%. Based on these reference studies, 38.50% of the vineyards had insufficient in terms of phosphorus content (Table 2). Yener et al (2002) [14] found this value as 64% in the vineyards of Kavaklıdere and Atalay et al (1991) [17] reported as 55% in the vineyards of Salihli, where in surrounding of the Plain of Alasehir.

When potassium contents of leaf (lamina) samples collected during the veraison period were evaluated according to Boulay et al (1984) [7] (1.11-1.40%), no nutritional problems in terms of potassium content in the vineyards were determined. Besides, there was no K deficiency in vineyards when the results of analysis were compared to the reference values (1.20%, 1.20-1.60%, 0.55-1.05%) suggested by Levy (1968) [5], Bergman (1988) [18] and Conradie (1986) [6] (Table 2). When potassium and nutrient condition of the vineyards were examined through K/Mg ratios, it was determined that K/Mg ratios of leaf samples varied between 2.04 and 3.00 during the veraison period (Table 2). When the K/Mg ratios of leaf samples were evaluated according to Levy (1968) [5], a slight potassium deficiency (K/Mg = 1.50-2.00) was determined only in vineyard sample G. On the other hand, based on the previous studies on vineyard soils nutrition profiles from this region, vineyard soils were rich in available P and were both poor and rich in available K [13]. Thus, it can be suggested that not only their amounts in the soil but, also plant factors such as plant type as well as the physical and chemical properties of soils have an impact on the nutritional element availability of the soils. When Ca contents of the leaves (lamina) were compared to the reference values stated by Conradie (1986) [6], Jung et al (1971) [19], and Bergman (1988) [18] (these values were 1.50-2.40%, 1.30-1.94%, 1.50-2.50%) the vineyards in our study were determined to be sufficiently fed in Ca (Table 2). Magnesium contents of leaf samples during the veraison period were evaluated according to Levy (1968) [5] Mg = 0.30%. Our results showed that the level of magnesium in all the vineyards was at a sufficient level (Table 2). Additionally, based on the reference values of 0.23-0.29%, 0.50-1.00% and 0.25-0.50% suggested by Chapman (1965) [15], Loue (1984) [20], and Mills and Jones (1996) [8], respectively no nutritional problems in terms of magnesium were determined in the vineyards. The soils of the vineyards, where the study was carried out, were found to be rich in Calcium and Magnesium, which is consistent with our leaf analysis results [13,14].

TABLE 3 - Micro element contents of leaf samples collected from vineyard plantations.

Sample	Fe (ppm)	Zn (ppm)	Mn (ppm)	Cu (ppm)	B (ppm)
1	103.50	21.62	36.57	9.55	33.05
2	92.70	20.84	35.34	8.97	31.93
3	92.64	21.70	35.86	8.74	32.40
4	124.80	22.52	54.26	10.25	42.21
5	120.30	26.34	35.64	9.58	81.03
A	127.45	21.40	48.25	10.64	53.60
B	94.25	21.72	35.70	10.50	52.26
C	96.54	21.87	46.84	10.75	52.33
D	117.12	22.22	49.72	10.38	54.93
E	158.65	24.50	56.49	16.70	51.05
F	129.34	26.74	52.72	14.62	70.64
G	136.44	26.67	54.34	13.59	59.10
H	135.86	26.83	59.25	14.34	53.54
Average	117.66	23.46	46.23	11.43	51.39

The minimum, maximum, and average values related to the micro element contents (Fe, Zn, Mn, Cu, and B) of the leaf samples collected from the vineyards were presented in Table 3. Based on these results, Fe, Zn, Mn, Cu, and B contents were in the range of 92 and 158 ppm, 20.84 and 26.83 ppm, 35.34 and 59.25 ppm, 8.74 and 16.7 ppm, 31.93 and 81.03 ppm, respectively. Fe analysis results of the study were compared to Beyers's (1962) [21] 60-180 ppm and Fregoni's (1984) [3] 100-250 ppm reference values for the leaf lamina during the veraison period. According to the reference values from these studies, all vineyards were sufficient in Fe Beyers (1962) [21]. However, if we consider the reference values by Fregoni (1984) [3], 30.80% of the vineyards (vineyards 2, 3, B, and C) had Fe deficiency.

There was insufficient Zn nutrition in the vineyards based on the reference values of Reuter and Robinson (1986) [16] (15-26 ppm) and Beattie and Forshey (1954) [22] (20-30 ppm). In these studies, Zn contents were also determined in the samples obtained during the veraison period. When compared to reference values of 30 - 60 ppm suggested by Robinson (1990) [12] for leaf lamina, Zn deficiency was determined in all the vineyards. Thus, it can be concluded that it would be better to take the reference values suggested by Reuter and Robinson (1986) [16] and Beattie and Forshey (1954) [22] into consideration for evaluating the nutritional status of vineyards in terms of Zn. In general, our results of this study confirm the results from the previous studies which had previously been carried out in the vineyards in the same location (Alaşehir) [2,14].

For Mn levels, Reuter and Robinson (1986) [16] suggested 20-25 ppm and Bergman (1988) [18] 30-300 ppm as reference values. If we compare the Mn contents of the leaf lamina samples collected during the veraison period with the reference values of 25-200 ppm suggested by Robinson (1990) [12], we can conclude that all the vineyards had sufficient in Mn contents (100 %) (Table 3). Copper (Cu) content during the veraison period has been reported as 5-20 ppm by Fregoni (1984) [3], 6-12 ppm by Bergman (1988) [18], and 3-6 ppm by Reuter and Robinson (1986) [16]. As listed in Table 3, Cu values determined in this study were between the reference values given by different researchers above. The results for the Fe, Zn, Cu, and Mn matched with previous studies on soil nutrition profiles of the vineyards located in Alasehir [13,14]. Yener et al (2002) [14] reported 27-216 ppm Mn values and 13-110 ppm for and Cu contents in the leaf lamina during the veraison period. Secer et al (2002) [23] performed a research to examine the micro elements and heavy metal contents of different vegetables and fruits grown in Gediz basin. They found the Fe, Zn, Mn, Cu, and B contents of the leaf samples collected from the vineyards as 58.3-93.2 ppm, 16.8-50.5 ppm, 24.4-39.1 ppm, 8.9-48.8 ppm, and 304-381 ppm, respectively.

As shown in the Table 3, boron content of the leaf samples during the veraison period was found to be between 31.93 and 81.03 ppm (average 51.39 ppm). Based on the reference values by Mills and Jones (1996) [8], 92.31% of the samples had enough B content and 7.69% of the samples had B deficiency (Table 3). Yener et al., (2002) and Elmacı et al., (2002) [24] determined the similar B contents in their previous studies which were performed in the district of Alasehir. Furthermore, in a similar study carried out by Konuk and Yener (1995) [25] in the same location, it was determined that there was high boron content in the 88.64% of the groundwater (from wells) in the location. Boron contamination was determined in the 39.74% of the soils. Boron toxicity was reported in the 90% of the local vineyards. Through the studies carried out in the Plain of Alasehir, it was suggested that the water quality was very low. Therefore, this could harm to the vineyards where low quality water was used and boron accumulation could occur in the soils [26,27]. The reason for the high boron content in waters in the location might be due the presence of hot spring water in the region that could affect the composition of groundwater.

3.2 Some heavy metal contents (Cd, Co, Cr, Ni, and Pb) of the leaf samples

Minimum, maximum, and average values regarding heavy metal contents (Cd, Co, Cr, Ni, and Pb) of leaf samples collected in the vineyards are presented in the Table 4. According to the results of the analysis, the minimum and maximum values of Cd, Co, Cr, Ni, and Pb in leaf samples range between 0.28-0.38 ppm, 0.48-1.06 ppm, 0.51-1.07 ppm, 1.58-2.36 ppm and 2.60-5,31 ppm, respectively.

TABLE 4 - Some heavy metal contents of leaf samples collected from vineyard plantations.

Sample	Cd (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Pb (ppm)
1	0.31	0.57	0.55	1.65	3.12
2	0.28	0.48	0.52	1.58	4.17
3	0.28	0.48	0.51	1.62	2.60
4	0.31	0.72	0.74	1.92	4.20
5	0.32	0.93	0.80	1.78	4.00
A	0.31	0.87	0.52	2.04	4.70
B	0.30	1.06	0.53	1.95	5.07
C	0.30	0.91	0.70	1.97	5.05
D	0.34	0.84	1.07	2.17	4.65
E	0.36	0.76	0.91	2.14	4.33
F	0.36	0.55	0.88	2.23	5.00
G	0.37	0.64	0.84	2.36	5.22
H	0.38	0.59	0.85	2.12	5.31
Average	0.32	0.72	0.72	1.96	4.42

While Mengel and Kirkby (1987) [4] suggested the 0.10-1.00 ppm of cadmium (Cd) in plants as normal value, Scheffer and Schachtschabel (1989) [28] reported this value as 0.04-0.50 ppm. Bowen (1979) [29] suggested that plants could contain 0.10-2.40 ppm of Cd. Kloke (1980) [30] stated that high crops could contain 0.20-0.30 ppm of Cd. Sauerbeck (1982) [31] gave the reference value of 5-10 ppm of Cd for the plants. Secer et al (2002) [23] found

Cd as 0.25 ppm in their study, in which they examined the micro element and heavy metal contents of different fruit and vegetable leaves in Gediz basin. Tuna et al (2005) [32] determined the Cd in olive leaves as an average of 0.28 ppm in the research, which was performed in order to determine the pollution that arises from the thermic centrals (Gökova, Yeniköy, Yatağan) in the vicinity of Muğla. Austanfeld (1979) [33] found the Cd toxicity in plants as between 5-10 ppm. Taking these data into consideration, it can be concluded that there is no Cd pollution in the vineyard leaves investigated in this study.

In the previous studies, Cobalt (Co) qualified as micro nutrition element or a useful element existed in the structure of B12 vitamin in the animal organism [18]. Scheffer and Schachtschabel (1989) [28] suggested that Co usually existed in plants between 0.02-0.50 ppm. Nichol and Beckett (1985) [34] reported that Co concentration which can cause 10% yield depression of in plants was between 4 and 40 ppm. Sauerbeck (1982) [31] gave the toxic levels of Co on plants as 10-20 ppm. Based on these studies, we can make the assumption that there was Cd toxicity in the location where our study was conducted (Table 4). It is a well-known fact that factors such as the pH of the soil, the amount of the soil, mug, the content of organic materials, and the kind of the plant as well as the total quantity of the heavy metals have an effect on the heavy metal uptake of the plant from the soil [28,31]. Secer et al (2002) [23] reported that B, Cu, and Co pollution existed in the vineyards in different areas in Gediz basin (Alaşehir, Kemalpaşa, Manisa, Menemen).

Scheffer and Schachtschabel (1989) [28] determined normal Chrome (Cr) concentrations in soil as 0.10-1.00 ppm. Kabata-Pendias and Pendias (1992) [35] reported the critical Cr concentration as 5-30 ppm. Nichol and Beckett (1985) [34] explained the Cr concentration which would cause of 10% yield reduction in plants as 2-18 ppm. Cr concentrations that can be toxic in plants have been reported as 2-18 ppm by Sauerbeck (1982) [31]. According to these reports, if 1.00 ppm Cr is considered as reference value for the leaves, the Cr content does not consider in pollution level except in vineyard sample D. If 2.00 ppm Cr is considered as a reference value, the Cr content does not consider in pollution levels in the vineyards (Table 4). Additionally, there was Cr pollution reported in the soils of the vineyards in the area, which confirms the findings in this study.

Tuna et al (2005) [32] investigated the Cr levels in the samples from the leaves that were collected from fields around thermic centrals located in Gökova, Yeniköy, and Yatağan. The Cr levels were around 20 ppm. Bowen (1979) [29] reported that normal Nickel (Ni) concentration in plants was 0.02-5.00. Scheffer and Schachtschabel (1989) [28] also suggested that the Ni content in plants should be below 3 ppm under normal conditions. Sauerbeck (1982) [31] also mentioned that the critical value of Ni toxicities for plants was 20-30 ppm. If Scheffer and Schachtschabel's (1989) [28] and Bowen's (1979) [29] reference values are taken into consideration, it can be clearly explained that there is no Ni pollution in the vineyards studied in the area (Table 4). However, it was found that Ni pollution started in the soils where vineyard farming was being performed (examined vineyard soils). This result shows that the properties of soil and plant have been effective on heavy metal uptake. Altinbas et al (1994) [36] suggested that Ni toxicity did not exist in the leaves of the vineyards and peaches in the research they carried out in Gediz basin, which confirms the results in this study.

Scheffer and Schachtschabel (1989) [28] reported that it was acceptable for the plants to have 0.10-6.00 ppm of lead (Pb). Bowen (1979) [29] found that 0.20-2.00 of Pb could exist in plants. Sauerbeck (1982) [31] explained that the critical value for Pb in plants was 10-20 ppm. If 10 ppm of Pb is accepted as critical value, there is no Pb pollution in the vineyard plantations. Previous studies in this region also reported that there was no Pb pollution in the vineyard soils [23,36].

4. CONCLUSION

The heavy metal contents, macro and micro elements and the nutritional conditions of the plant leaf samples collected from the vineyards in the Plain of Alasehir were analyzed in this study. In terms of the macro element contents of the leaf samples, 15.0% and 38.5% of the vineyards were insufficient for N and P contents, respectively. All the vineyards were fed sufficiently for K, Ca, and Mg. It was also found that the 30.8% of the vineyards were insufficient in Fe. The leaves were sufficient in terms of Zn, Mn, and Cu contents.

As for Boron, the quality of the water in the Plain of Alasehir was low and harmful for the vineyards. Boron can accumulate in the vineyard soils. Additionally, this study proved that the fertilization programs should be incorporated into the region as part of the farming practices. When some heavy metal contents of leaf samples were examined, there was no Cd, Co and Pb pollution in all the vineyards. Additionally, there was no Cr pollution in the 93.20% of the vineyards; only vineyard sample D had Cr pollution.

The authors have declared no conflict of interest.

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FEB/ Vol 24/ No 4b/ 2015 – pages 1573 - 1578