Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4371-4388

Assessment of Heavy Metal Accumulation in the Soils and Hazelnut Plant (*Corylus avellena* L.) from Black Sea Coastal Region of Turkey

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For decades, heavy metal contamination due to traffic activities on roadside soils and crops has been one of the major concerns in developed and developing countries. Pollution assessment is the key factor to protect the ecological function and agricultural sustainability of soils. In order to investigate the extent of heavy metal contamination of roadside soil and hazelnut plant, 6 sampling sites, which were situated along the 010-17 motorway from Unye to Gulyali (Turkey), were selected. Soil and leaf samples were collected from 0-10, 11-20, 21-30, 31-40, 41-50, 51-100, 101-200 and 201-400 m altitudes for each of the sampling sites. Total and available heavy metal concentrations in soil and hazelnut leaves were determined using ICP-OES after digestion. The concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in total and available forms in the soil and plant leaves were decreased with the increase of altitude at different rates. This data can be used to distinguish between sources of pollutant (traffic activity, agricultural, natural activities). Hence it is clear from the results that Pb, Cd and Ni contamination of roadside soils was contributed mainly from traffic activities and Cu and Zn were mainly due to agricultural activities as evidenced by their distribution patterns and their enrichment factors (EF). The enrichment value for distinguishing the accumulation of elements in the lower altitude location from the traffic activities to agricultural activities and natural erosion is about 1.5. However, the concentrations of these elements in hazelnut leaves were negligible. The concentration of most determined elements in this study area are better related to soil total concentration is linear (Cd, Fe, Ni, Pb and Zn) or quadratic (Co and Cr) relationship to soil available concentration except Mn and Cu which are better related to the later form.

Key Words: Heavy metal pollution, Hazelnut, Traffic pollution, Enrichment factor.

INTRODUCTION

Soils of several regions of the world is being exposed to fertilizer and pesticide applications, industrial and municipal pollution and road and infrastructure expansions.

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All these activities affect the physico-chemical properties of soils leading to behaviourial changes in soil trace elemental composition. Trace metal uptake by vegetation has already become serious environmental and health concern[1]. Contamination of roadside soils with heavy metals occurs from various pollutant sources such as vehicles, road wear and slipperiness control additives. Trace metals such as, Cd, Cu, Zn and particularly Pb in surface soils by roadside pollution have been the focus of recent investigation[2]. Accumulation of these metals in surface soil is greatly influenced by the traffic volume and automobile type, which infuse numerous toxic metals to the atmosphere[3-6]. The bioavailability and environmental mobility of these metals depend largely on their existing forms in soils. Pollutants emitted from automobiles are higly diverse. Fossil fuel contains several types of heavy metals that are emitted to the environment inevitably during the combustion[7,8]. The wear of auto tires, degradation of automobile parts and greases, peeling of the external paint and metals in catalysts are also suspected sources of heavy metal pollution[9-11]. It is well known that automobiles are not only responsible for the dispersion of previously listed heavy metals (Cu, Zn and Pb), but also a few other hazardous elements.

Hazelnut (*Corylus avellena* L.), belonging to *Betulaceae*, is a popular nut tree worldwide. This tree is distributed mainly in Black Sea coastal regions of Turkey, Southern Europe (Italy, Spain, Portugal, France and Greece) and in some areas of the United States of America (Oregon and Washington). Turkey (as termed Anatolia-the genetic origin of hazelnut), is naturally suited for growing hazalnuts and cultivates maximum number of wild species (20 varieties). Turkey is also world's major hazelnut producer and exporter contributing to about 74 % of the total global production[12].

In past few years, the vehicular traffic in Turkey has increased rapidly resulting in heavy metal contamination of soils and plants closer to highways, both in urban and rural areas. Most of the available literature on the concentration of heavy metals in roadside soils and plants are from the developed countries. To best of our knowledge, no attempts for assessing the heavy metal accumulation in Turkey soil or hazalnuts were made. Such a study will be important considering the economic benefits and existing export potential for hazalnuts. The major objective of this study was to assess the heavy metal concentration in hazalnuts and soils nearby motorway and inland of Black sea coastal areas as a factor of altitude from the road.

EXPERIMENTAL

Northern part of Turkey was selected as a study area for assessing the heavy metal concentrations in soil and hazelnut. Soil type of this area was classified as alfisol[13]. Mean annual temperature, precipitation (rainfall) and relative humidity were 13.8 ºC, 1183 mm and 74.7 %, respectively. Wind direction usually is S-WSW[14].

Six sampling locations were selected for detailed analyses. These points were situated along 010-17 motorway connecting Unye to Gulyali city. These sampling points were selected after a preliminary survey carried out during 2006 (Table-1).

TABLE-1
TRAFFIC COUNTS, COORDINATES, LOCATION ALTITUDES AND MANAGEMENT GROUPS FOR SELECTED STUDY SITES

Study site	Total number of vehicles per month	Sampling altitude (m)	Coordinates	Management group #
Unye	54,500	0-10 11-20 21-30 31-40 41-50 51-100 101-200 201-400	35º15.300' E-45º56.373' N 37º03.530' E-45º46.585' N	3A
Fatsa	54,500		37º90.610' E-45º42.739' N 39º64.800' E-45º52.288' N	3B
Boztepe	54,500		40º30.210' E-45º36.769' N 40º49.940' E-45º37.010' N	4A
Ordu	51,200		41º41.550' E-45º36.892' N 42º14.790' E-45º35.512' N	4B
Persembe	51,200		38º42.550' E-45º48.136' N 39º81.510' E-45º51.779' N	5A
Gulyali	51,200		41º55.230' E-45º36.892' N 41º70.700' E-45º36.800' N	0 and 6A

#Level bottomland soils; 3A, Sloping, moderately eroded, deep and moderately deep soils; 3B, Sloping, moderately to severely eroded, shallow soils; 4A, Moderately steep, moderately eroded, moderately deep soils; 4B, Moderately steep, moderately to severely eroded, shallow soils; 5A, Steep, severely eroded, shallow soils; 6A, Very steep, severely to very severely eroded, shallow soils [Ref. 28].

Approximately, 1500 vehicles pass through this every day and this is a main road connecting Samsun to Trabzon city in the middle and eastern part of Turkey's Black sea coast. Soil and plant samples were collected from hazelnut gardens, that are located at 0-10, 11-20, 21-30, 31-40, 41-50, 51-100, 101-200 and 201-400 m altitude along the main road. The sampling point of 0-10 m started at 5 m distance from the edge of the motorway. For each altitude location, 10 surface soil (0-10 cm) and leaf samples (50 plant leaves per tree) were collected within a 2000 m^2 area. Soil and plant samples were carefully packed in separately polyethylene bags. All the soil samples were air-dried and ground to pass through 2 mm sieve for physico-chemical analyses. The soil properties analyzed were texture[15], cation exchange capacity (CEC)[16], Kjeldahl-N[17], available P[18], electrical conductivity (EC)[19], pH (1:2.5 H_2O w/v)[20], organic matter (OM)[21] and exchangeable Ca, Mg, K and Na[22]. The available (AMH) and total form (TMH) of elements namely, Fe, Mn, Zn, Cu, Ni, Pb, Cr, Al and Cd were determined using ICP-OES (Varian Vista-Pro, Australia) after DTPA extraction[23] and digestion in a closed vessel microwave system (CEM MarsExpress, USA) with HCl (37 %)-HNO_3 (65 %) - H_2O_2 (30 %) (3:1:1 v/v) solution[24], respectively. Basic soil physico-chemical properties are presented in Table-2. Plant samples were carefully washed with deionized water to remove adsorbed dust, oven dried for 48 h at 68 ºC and powdered. All the trace metals (same elements that were tested for soil samples) in hazelnut leaf were determined using ICP-AES after digestion in the closed microwave system with HNO_3 (65 %)[24].

RESULTS AND DISCUSSION

General properties of soils in the study area: Soil texture in sampling sites ranged from loam to clay loam. This is an optimally suited soil texture reported for hazelnut cultivation[25] (Table-2). The organic matter (OM) contents in soil varied

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF SOILS AT SELECTED SAMPLING SITES (0-10 cm DEPTH, n = 10, MEAN ± STANDARD DEVIATION)

Parameter	Persembe	Unye	Fatsa	Ordu	Gulyali	Boztepe
STC	CL	SCL	L	SL	SiCL	SiCL
Organic C	1.83±0.32	1.55±0.42	1.80±0.24	1.40±0.29	1.45±0.33	1.51±0.35
pH	5.25±0.70	5.42±0.40	5.30±0.40	5.72±0.80	5.60±0.50	5.80±0.50
Total N (g kg^{-1})	0.15±0.02	0.18±0.05	0.19±0.08	1.19±0.04	1.17±0.04	1.18±0.05
Mehlic III (mg kg^{1})	18.4±1.3	12.5±1.7	16.4±1.4	13.8±2.1	14.7±1.5	11.4±1.6
CEC ($cmol_{(+)}$ kg^{-1})	30.2±1.8	18.6±1.3	26.8±1.4	15.7±1.1	22.4±1.4	26.3±1.5
EC (dS m^{-1})	0.22±0.08	0.18±0.07	0.15±0.06	0.17±0.06	0.13±0.07	0.12±0.07
ECT ($cmol_{(+)}$ kg^{-1})						
Al	12.8±1.2	8.9±1.6	14.7±1.3	8.6±1.0	13.7±1.3	14.5±1.5
K	1.4±0.2	0.6±0.1	1.1±0.2	0.9±0.2	0.8±0.2	0.9±0.3
Ca	8.1±1.1	6.3±1.0	7.6±1.4	7.1±0.9	6.8±1.4	7.4±1.5
Mg	2.4±0.3	1.9±0.2	2.1±0.5	2.2±03	1.9±0.3	2.0±0.3
Na	0.2±0.05	0.2±0.03	0.3±0.06	0.2±0.04	0.2±0.05	0.2±0.04
AHM (mg kg^{-1})						
Zn	27.9±1.9	19.6±2.2	20.1±1.8	24.2±1.9	18.5±2.0	21.5±1.6
Mn	193±6	176±5	150±7	166±6	187±6	158±7
Fe	238±5	138±5	204±7	170±4	139±5	230±8
Cu	11.5±1.5	7.9±1.2	8.9±1.3	7.7±1.4	6.8±1.5	7.5±1.3
Cd	0.06±0.003	0.04±0.002	0.05±0.003	0.04±0.001	0.05±0.001	0.08±0.001
Pb	1.56±0.22	1.69±0.34	1.72±0.42	1.14±0.25	1.06±0.28	1.42±0.37
Cr	0.54±0.17	0.29±0.10	0.52±0.15	0.38±0.10	0.29±0.08	0.66±0.19
Ni	1.60±0.34	1.07±0.41	1.17±0.28	1.66±0.33	1.88±0.24	1.95±0.42
Al	173.0±4.1	102±4	147±3	128±3	82.0±1.7	169±3
Co	0.69±0.12	0.74±0.23	0.41±0.17	0.47±0.15	0.38±0.11	0.33±0.12
THM (mg kg^{-1})						
Zn	350±11	270±13	311±11	335±16	285±10	291±12
Mn	520±15	584±14	499±18	511±20	524±14	467±18
Fe	768±19	820±23	736±18	755±20	725±19	742±22
Cu	221±9	206±9	213±9	224±11	230±9	228±9
Cd	2.18±0.66	2.05±0.75	1.99±0.33	1.87±0.39	2.12±0.42	2.40±0.37
Pb	90.5±4.5	88.6±5.3	82.8±6.8	84.3±4.7	75.7±5.3	88.6±4.8
Cr	41.2±1.3	39.6±1.4	45.4±1.1	38.7±1.8	42.4±1.2	35.6±1.3
Ni	18.3±2.11	15.2±1.13	16.4±2.10	12.3±2.15	15.5±2.13	14.9±1.15
Al	3865±108	4100±1114	4210±97	3766±112	4218±124	4066±113
Co	9.66±1.65	8.85±1.47	11.4±2.3	10.7±2.2	8.90±1.95	9.60±1.78

PSD = Particle size distribution, STC = Soil texture class (US System), pH: (1:2.5 soil:water), CEC = Cation exchange capacity, EC = Electrical conductivity, ECT = Exchangeable cations, AHM = Available heavy metal (DTPA extract solution), THM = Total heavy metal.

from 2.9-6.7 %. The high soil OM content may be due to historic accumulation of plant residues as this area was covered by forest. Moreover the existence of humid climatic conditions supports accumulation of more organic matter by trees which eventually fall onto soil surface to enrich soil organic matter. Soil pH was in the acidic range, was in the optimum of 5.5-7.0 suggested for hazelnut cultivation by Genc[25] and was almost constant throughout the study area. Soil cation exchangeable capacity (CEC) varied between 15 and 30 cmol (+) kg^{-1} representing medium rank in soil evaluation rating[26]. The concentration of available phosphorus in the soil was at the lower range[27], while magnesium and potassium were at fertile ranges[26]. The variations in total heavy metal composition of soils among six locations were almost similar. Most of their coefficients of variation (CV) were less than 10. Thus in order to have generalized information on the distribution of heavy metal with increase in altitude, the data obtained in all the six selected locations were pooled based on the altitude. According to the report published recently by a management group affiliated to Turkey government[28], the erosion levels in the study site was classified as moderate to severe, therefore the accumulation of all determined elements in the lower altitude area was expected to be reasonable/higher and the accumulation extent of each element was also evaluated in this study.

Distribution of heavy metals in soil and plant leaves: The distribution of total and available elemental concentration in soils is presented with reference to the altitude in Figs. 1-10. The concentration of both forms of each element in soil decreased with increased altitude while the decrease of a few elements was more drastic than the others. In addition, the relationships between the elements were described by the following equation:

$$\ln Y_{CE} = \ln A1 + B1/X_{AL} \quad (1)$$

$$\ln Y_{CEM} = \ln A2 + B2\ X_{AL} \quad (2)$$

where Y_{CE} is the concentration of elements in soils (total or available). X_{AL} is the altitude of sampling. A1, B1, A2 and B2 are constants. The value of A1 in eqn. 1 illustrates the value of that element reached a constant level (*i.e.*, the lowest level). This value can be taken as a background concentration of an element in a soil which has no uneven balance on that land. In the study this value was used as one of the parameters employed to evidence that whether an accumulation of an element occurred in this area no matter the sources were from the natural or anthropogenic activities (Table-3). In this area, the accumulation of elements in the lower altitudes might be from traffic pollutants or carried due to erosion from the upper altitude fields. The values of B1 and B2 can be used to describe the rate of decrease of an element with the increasing altitude. The mean of the sampling altitude was used in this regression fitting, for example 5.0 m presents the location ranged at 0-10 m altitude. The regression data including the statistically significant levels of each coefficient and R^2 are shown in Table-3. The highest concentration of each element was in the 0-10 m altitude area, the most close to the motorway. Some elements

TABLE-3
RELATIONSHIP BETWEEN THE CONCENTRATION OF ELEMENTS IN SOILS AND THE LOCATION ALTITUDES OF THE STUDY AREA

Elements and forms	ln Y = ln A1+ B1/X			ln Y = ln A2 + B2 ln X		
	ln A1	B1	R^2	ln A2	B2	R^2
Al						
Available	Y = 1175-2.92 X		0.938‡			
Total	8.33‡	0.158*	0.648*	8.38‡	-0.0093‡	0.896‡
Cd						
Available	-3.42‡	3.5*	0.591*	-2.49‡	-0.204†	0.796†
Total	0.915‡	4.98†	0.718†	2.20‡	-0.281‡	0.910‡
Cr						
Available	-3.60‡	4.83*	0.598*	-2.25‡	-0.300‡	0.915‡
Total	3.72‡	2.51‡	0.966‡	-4.12‡	-0.124†	0.831†
Co						
Available	-0.420	6.71*	0.568*	1.50‡	-0.426‡	0.913‡
Total	2.32‡	2.28‡	0.897‡	2.84‡	-0.110†	0.828†
Cu						
Available	0.964‡	4.619†	0.717†	2.19‡	-0.269‡	0.969‡
Total	5.42‡	1.14‡	0.915‡	5.65‡	-0.0487*	0.664*
Fe						
Available	5.02‡	2.01*	0.682*	5.56‡	-0.118‡	0.938‡
Total	6.74‡	1.17†	0.823†	7.00‡	-0.054*	0.694*
Mn						
Available	4.24‡	4.54	0.468	5.64‡	-0.316‡	0.903‡
Total	6.32‡	1.19†	0.726†	6.59‡	0.58*	0.692*
Ni						
Available	-0.660*	3.17	0.220	0.485	-0.266*	0.617*
Total	3.05‡	2.80‡	0.872‡	3.69‡	-0.134†	0.790†
Pb						
Available	0.572†	6.53*	0.684*	2.34‡	-0.389‡	0.968‡
Total	5.20‡	8.58	0.439	7.84‡	-0.598†	0.847†
Zn						
Available	0.285*	5.79†	0.745†	1.27*	-0.191	0.312
Total	5.87‡	0.762‡	0.865‡	6.03‡	-0.0339*	0.681*

#Excluded 21-30 m altitude data (n = 7).
*Statistically significant, $p < 0.01$; †$p < 0.05$; ‡$p < 0.001$.

(Cr, Cu, Fe and Zn) decreased rapidly with increase in altitude (*i.e.* away from the roadside) and reached a constant level after a location altitude (at different altitudes for different elements), while other elements did not reach a constant level in this study area. The first rapidly decreasing elements were Fe, Cr, Zn and Cu and their concentration reached a constant level at 21-30 m altitude, followed by Mn at 31-40 m, Ni at 41-50 m, Cd and Co at 51-100 m and Al and Pb at 101-200 m.

The distribution pattern of total elemental concentration can be used to predict the source of enrichment of an element (traffic pollution, farming practices or natural erosion) is discussed herein. The enrichment factor (EF) ($EF_{soil} = (M/Fe)_{soil}/(M/Fe)_{control}$) can also be used as an index to distinguish whether the accumulation of particular element in soils is derived from natural or anthropogenic sources. According to Olivia and Espinosa[29], the EF value > 2 can be considered as a critical level for an enrichment contributed mainly by anthropogenic inputs.

Aluminum: Aluminum is most abundant in soil and is not an essential nutrient to most of the plants. Although accumulation of this metal was predicted to be by the traffic pollution especially to a component in catalytic mufflers of vehicals[30], there is no conclusive evidence to link directly its pollution to roadside soil[10,31]. Total Al concentration in soil decreased with the increased altitude of 101-200 m (Fig. 1).

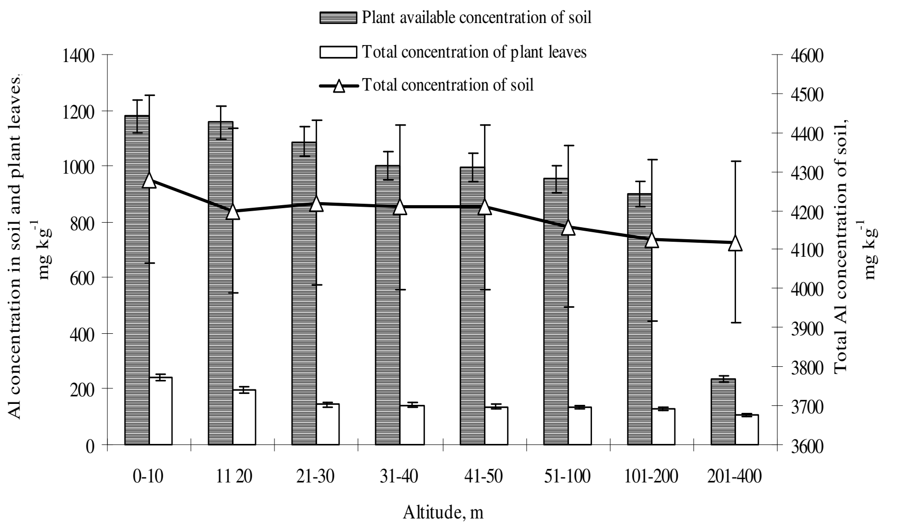

Fig. 1. Distribution of concentration of Al in soil total and available forms and hazelnut leaves with location altitude

The changes in total soil and leaf concentration of Al in relation to altitude could clearly be resolved using equation 2 than eqn. 1 (Table-3). This result indicates that, although the concentration of this metal was highly related to altitudal change, it failed to reach a soil constant level. The available Al concentration (Y_{ALA}) decreased lineraly with the increase in altitude (X_{AL}), $Y_{ALA} = 1175 - 2.92\ X_{AL}$, ($R^2 = 0.938$, $p < 0.001$). The accumulation of Al in lower altitude soil could be visualized clearly in Fig. 1, but all the EF values were in narrow range (1.02 to 1.06) (Table-4). This may be due to the presence of high concentration of Al in the sampled soil, which might have deposited due to upper altitudal erosion.

Cadmium: Cadmium, a trace element present generally is toxic to plants, animals and humans in higher concentrations. Previous studies related the higher levels of Cd to vechicular traffic emission[32,33] or tyre wear[34], but again, there are no conclusive evidences to prove that the Cd pollution in the roadside soil is mainly from the traffic activities[10,29].

TABLE-4
ENRICHMENT FACTOR (EF) OF TOTAL CONCENTRATION OF ELEMENTS DETERMINED AT EACH LOCATION ALTITUDE IN THE STUDY AREA

Locations (m)	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0-10	1.06	2.79	1.57	1.65	1.27	1.39	1.32	2.29	8.00	1.34
11 20	1.04	2.22	1.34	1.29	1.16	1.30	1.24	1.95	6.56	1.26
21-30	1.05	1.82	1.13	1.12	1.04	1.12	1.22	1.54	6.17	1.17
31-40	1.04	1.50	1.12	1.09	1.04	1.14	1.06	1.52	5.20	1.16
41-50	1.04	1.48	1.11	1.05	1.04	1.16	1.06	1.41	3.78	1.18
51-100	1.03	1.02	1.02	1.04	1.04	1.13	1.06	1.36	1.42	1.17
101-200	1.02	1.02	1.02	1.04	1.03	1.11	1.06	1.36	1.12	1.18
201-400	1.02	1.02	1.02	1.01	1.04	1.12	1.07	1.36	1.10	1.14

Total concentrtion of Cd in the soils at 0-10 to 41-50 m altitude (ranged from 3.1-5.8 mg kg^{-1}, Fig. 2) was higher than the ICRCL[35] trigger level (3 mg kg^{-1}), but far less than the action level (15 mg kg^{-1}). The total concentration of Cd in soil decreased steadily with the increased altitude, described at highly significant and most highly significant level by eqns. 1 and 2, repectively (Table-3) and reached a constant level at 51-100 m (Fig. 2). Eqs. 1 and 2 also can be used for describing the changes in available Cd in soil with increased altitude at significant ($p < 0.05$) and highly significant ($p < 0.01$) levels, respectively (Table-3). The accumulation of Cd in soil might be from the traffic activies, erosion deposition or agricultural activities. In Netherlands, researches found that the contribution of Cd into arable land from fertilizer input was higher than atmospheric deposition and concluded that phosphate and compound fertilizers were the major contributors[36]. The EF values of Cd ranged from 1.02 to 2.79 (Table-4) and increased as the roadside approached (Fig. 2).

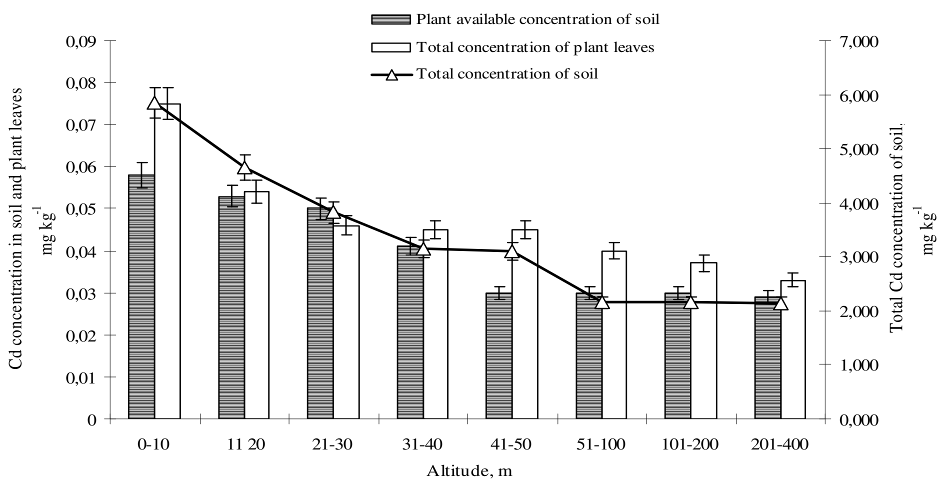

Fig. 2. Distribution of concentration of Cd in soil total and available forms and hazelnut leaves with location altitude

This gives a strong indication that, traffic activities will be an important contributor of Cd pollution in the roadside soils. However, without an elaborate investigation it may not possible to estimate the extent of enrichment due to traffic activities and farming activities or natural erosion. Although the concentration of Cd in hazelnut leaf (Y_{CdL}) is highly linearly related to soil total Cd concentration (X_{CdTS}): $Y_{CdL} = 0.0156 + 0.00926\ X_{CdTS}$, $R^2 = 0.913$, $p < 0.001$. The concentration of Cd in the hazelnut leaves was very low and usually the concentration of Cd in fruit was lower than that in leaves. Thus the hazelnut produced in this area is in a safer limit.

Cobalt: Cobalt, a non-essential nutrient for plants, but is required in trace amounts by nitrogen fixing microorganisms that have a symbiotic relationship with legumes. Vitamin B_{12} has 4 % of cobalt in its chemical constition. It is considered as one of the potentially hazardous element. Efroymson *et al.*[37] suggested that its phyto-toxic concentration was 20 mg kg^{-1}, while the ERD[38] set the ecological soil screening level at 13.4 mg kg^{-1}. The concentraion of soil total Co of samples at 0-10 (15.5 mg kg^{-1}) and 11-20 m (13.2 mg kg^{-1}) altitudes was near the trigger values (Fig. 3).

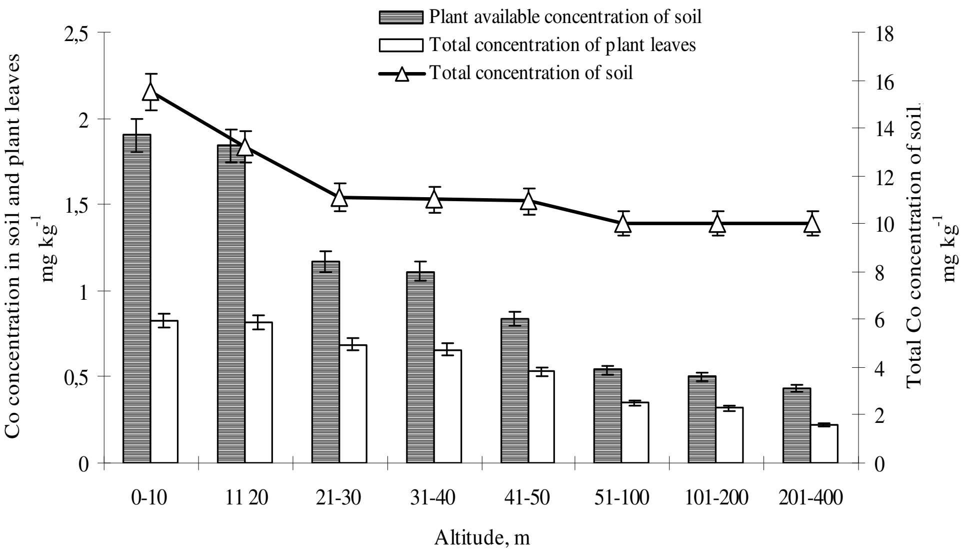

Fig. 3. Distribution of concentration of Co in soil total and available forms and hazelnut leaves with location altitude

The Netherland government has set the target value for Co for garden soil at 20 mg kg^{-1}. The decrease in total soil Co concentration with the increase in altitude can be described by eqns. 1 and 2 (Table-3) at most highly significant and highly significant levels, respectively. Cobalt concentration reached a constant level at 51-100 m altitude. However, the eqn. 1 describing the relationship between concentration of available Co with height of altitude was significant at $p < 0.05$, while eqn. 2 was significant at $p < 0.001$ level. The EF values of Co ranged from 1.02 to 1.57 (Table-4) and increased towards roadside (Fig. 3). This gives a strong evidence to conclude that the accumulation of Co existed in this area. There are no reports suggesting the release of Co by traffic activities in the roadside soils. Thus the enrichement (EF) of Co at the lower altitude could be due to the deposition of soil erosion from the higher areas. The concentration of Co in hazelnut leaf (Y_{CoL}) is lower than 0.9 mg kg^{-1} (Fig. 4) and is highly related to soil total Co concentration (X_{CoTS}): $Y_{CoL} = -6.72 + 1.10\ X_{CoTS} - 0.0396\ X^2_{CoTS}$, $R^2 = 0.920$, $p < 0.001$.

Chromium: Chromium is required in trace amount for animals and humans and is toxic in its Cr(VI) form. Monaci *et al.*[10] investigated the accumulation of Cr in soil besides the busy road, but could not correlate it with traffic activities. The total concentration of Cr in soils (ranged from 35.6 to 66.7 mg kg^{-1}, Fig. 4) and is much lower than the ICRCL[35] trigger level (600 mg kg^{-1}). The Cr concentration remains constant after 21-30 m altitude from eqns. 1 and 2. The EF value of Cr ranged from 1.01 to 1.64 (Table-4) and was increased towards roadside. This result indicates similar to Co that, the accumulation of Cr is present in this area and both of these elements are not by products of traffic pollutants. The EF value of Co and Cr can be of critical value to distinguish the pollution from the erosion to traffic activities. The concentration of Cr in hazelnut leaf (Y_{CrL}) is lower than 0.8 mg kg^{-1} (Fig. 4) and like Co is highly related to soil total Cr concentration in quadratic relationship (X_{CrTS}): $Y_{CrL} = -2.83 + 0.115\ X_{CrTS} - 0.00091\ X^2_{CrTS}$, $R^2 = 0.969$, $p < 0.001$.

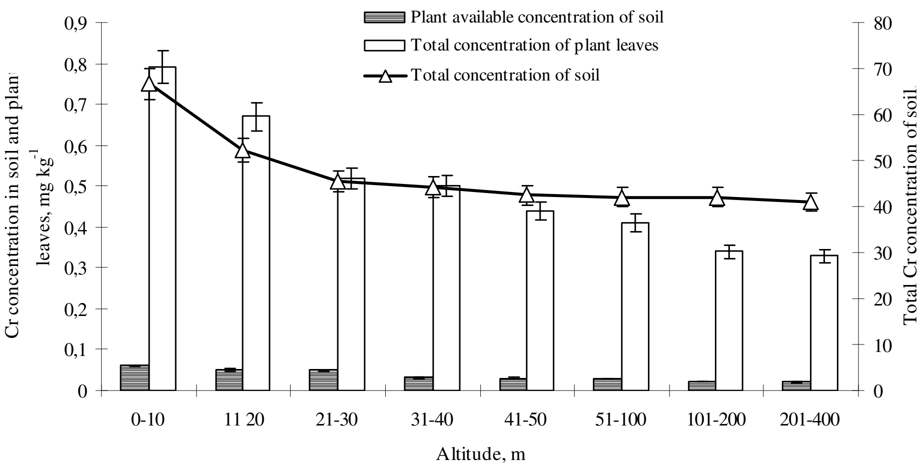

Fig. 4. Distribution of concentration of Cr in soil total and available forms and hazelnut leaves with location altitude

Copper: Copper is considered as toxic element to all organisms in higher quantities. The toxic trigger concentration is set at 130, 70 and 100 mg kg^{-1} by ICRCL[35], ERD[36] and Efroymson *et al.*[37], while the Netherland government set its target level[39] at 36 mg kg^{-1}. The concentraion of total Cu in all the soil samples (ranged from

221-280 mg kg^{-1}) in this study area was in toxic level. However the trigger level for different crops are different and the Cu concentraion of the hazelnut leaves were far lower than the data obtained[25] and only the highest concentration at 5-10 m altitude was higher than the data[40]. The concentration of Cu in hazelnut leaf (Y_{CuL}) is better related soil availble Cu concentration (X_{CuAS}): $Y_{CuL} = 6.04 + 0.802 X_{CuAS}$, $R^2 = 0.959$, $p < 0.001$.

There are strong evidences to suggest that traffic activities is one of the major Cu pollution source on roadside soils[10,30,34,41-44]. However, the drift of this particulate matter reaching higher altitude (201-400 m altitude) is yet to be proved. The distribution of total Cu concentration with altitude can be described better by eqn. 1 than eqn. 2 (Table-3) and the concentration reaches to a constant level at 21-30 m altitude (Fig. 5). This result indicates that, the Cu pollution of soils close to the motorway is caused mainly due to traffic activities. But the pollution from the use of fertilizers and manures for hazelnut cultivation[36] cannot be completely ruled out. The EF values of Cu ranged from 1.01 to 1.27 (Table-4) and was increased towards roadside approach (Fig. 5). The EF factor for Cu cannot be a good factor used as an indicator to judge pollution status. The total Cu concentraion of soils in this area is already higher than the legally allowed limits, but the EF factor is lower than 2[29] to distinguish the pollution source from the traffic activities to natural source. Obviously the Cu concentration of soils in this study area shows the polluted status, but the EF value is lower than the EF factor for Cr and Co. Hence it is reasonable to conclude that the pollution source of Cu in this area was mainly due to farming activities.

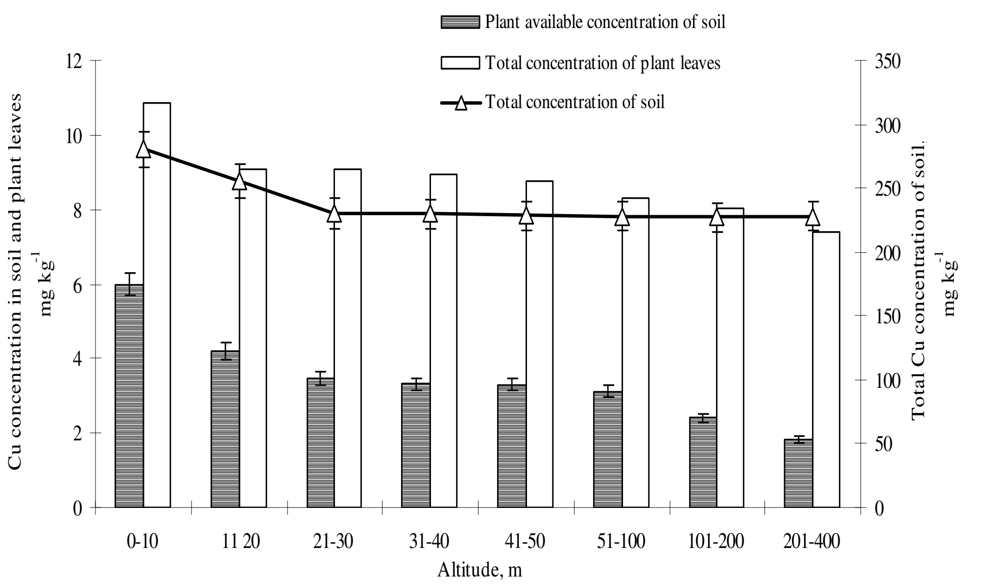

Fig. 5. Distribution of concentration of Cu in soil total and available forms and hazelnut leaves with location altitude

Iron: The leaded petrol and diesel oil contain higher levels of Fe, while it is also present in lower quanities in unleaded pertol emission[30,41,43]. Some reports showed that the traffic activities enriches the roadside soil Fe content[10,42,44,45]. However, Oliva and Espinosa[29] concluded that the enrichment of Fe in roadside soil was due to natural sources. The decrease of concentration of soil total Fe with the increase in altitude is described better by eqn. 1 (Table-3). The Fe concentration reached a constant level at 21-30 m altitude (Fig. 6). This suggests that the effect of the soil near the main road is polluted by traffic activities. The concentrations of Fe in the samples of hazelnut leaves were lower than the data recorded[25,40]. Although Fe has been cited as a component in petrols and oils used for cars, but higher amount of Fe recorded in present study may be due to inherent Fe present in soil and this is easily transformed into steady forms. The EF factor in this area was not high (ranged from 1.12 to 1.39) (Table-4). The concentration of Fe in hazelnut leaf (Y_{FeL}) is highly linearly responded to soil total Fe concentration (X_{FeTS}): Y_{CdL} = -360 + 0.637 X_{FeTS}, R^2 = 0.918, $p < 0.001$.

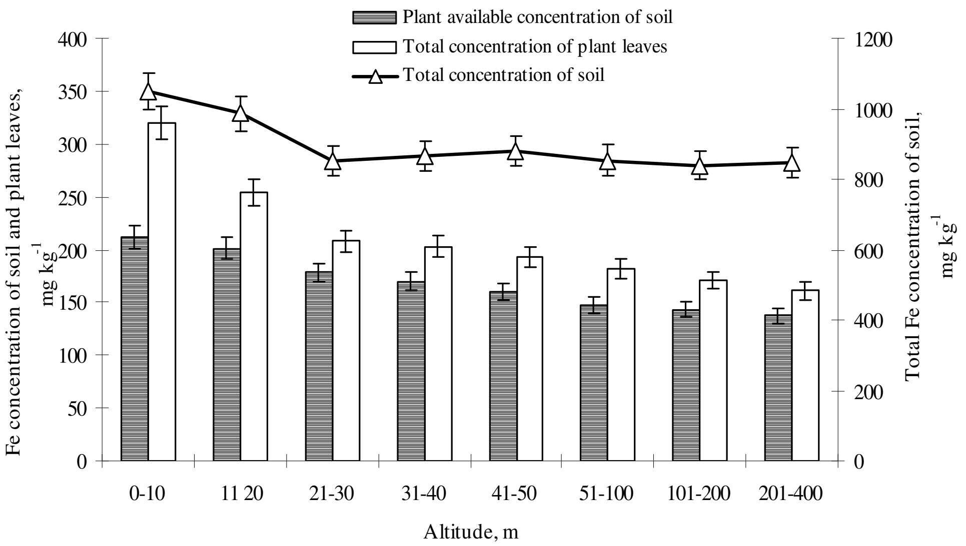

Fig. 6. Distribution of concentration of Fe in soil total and available forms and hazelnut leaves with location altitude

Manganese: Some reports showed that traffic activities enriched the Mn content in roadside soils[10,42,44,45], but Oliva and Espinosa[29] attributed this enrichement to natural sources. In general there is no toxic problem for upland crops, but ERD[38] has set the phytoxic level at 220 mg kg^{-1} for Mn. The toxic trigger concentration is set at 70, 38 and 300 mg kg^{-1} by ICRCL[35], ERD[38] and Efroymson *et al.*[37], while Netherland government set Mn target level[39] at 35 mg kg^{-1}. Accordingly, the concentraion of total Mn present in all soil samples (ranged from 548-685 mg kg^{-1}) in this study collected from 0-10 to 41-50 m location altitudes was higher than the data of Aydeniz *et al.*[25], but was lower in all samples compared to Painter and Hammer[40]. The decrease of soil total Mn concentration increases in altitude was described by eqns. 1 and 2 was significant at $p < 0.01$ and $p < 0.05$, respectively (Table-3). Manganese concentration reached to a constant level at 31-40 m altitude (Fig. 7). This suggests that the soils near the main road were seriously contaminatd by traffic activities. The change in available soil Mn concentrations with increase in altitude is better described by eqn. 2 at highly highly significant level (Table-3) than by eqn. 1. Although Mn like Fe has been cited as a component of petrols and oils used in cars, but it is also present in soil and easily transformed into steady forms. The concentration of Mn in hazelnut leaf (Y_{MnL}) is better correlated with soil available Mn concentration (X_{MnAS}): $Y_{MnL} = -204 + 1.48\ X_{MnAS}$, $R^2 = 0.957$, $p < 0.001$.

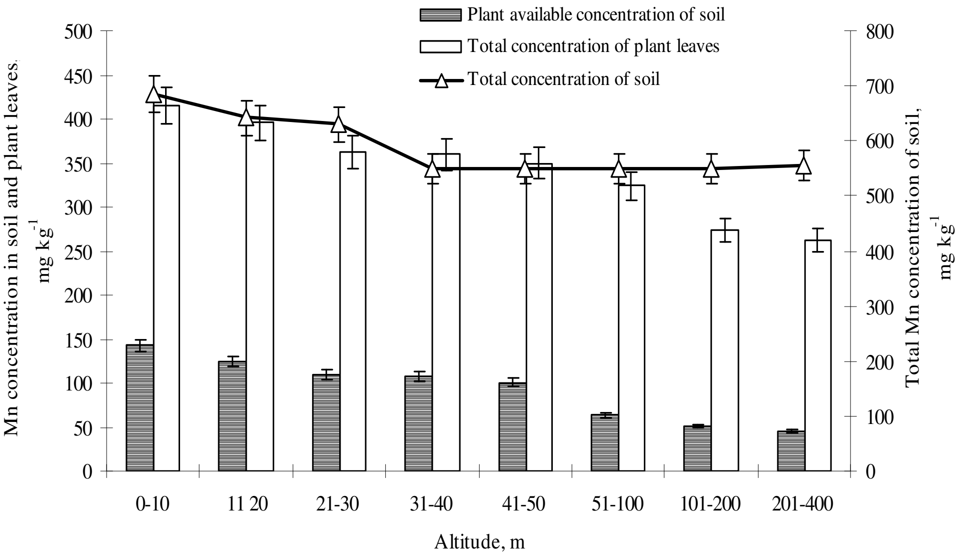

Fig. 7. Distribution of concentration of Mn in soil total and available forms and hazelnut leaves with location altitude

Nickel: Nickel, an essential element for animals and few plants is a trace element present in most soils. Some reports found that it was enriched in roadside soils but no direct evidence to conclude that enrichment was mainly from the traffic activities[10,29], although it was found in fossil fuel emissions[46]. The toxic trigger concentration of Ni in soil was set at 70, 38 and 300 mg kg^{-1} by ICRCL[35], ERD[38] and Efroymson *et al.*[37], respectively, while Netherland government set its target level[39] at 35 mg kg^{-1}. The concentration of total soil Ni in all the samples ranged from 21 to 35.3 mg kg^{-1} (Fig. 8). Only one of the present sample concetration (0-10 m altitude) was higher than the Netherland's target level. The concentration of Ni (Y_{NiL}) in hazelnut leaves was very low, ranged from 0.99 to 2.74 mg kg^{-1} (Fig. 8) and highly linearly related to soil total Ni (X_{NiTS}) concentration: Y_{NiL} = -0.707 + 0.0944 X_{NiTS}, R^2 = 0.821, $p < 0.01$. The decrease in total soil Ni concentration with increase in altitude was described better by eqn. 1 ($p < 0.001$) than by eqn. 2 ($p < 0.01$) (Table-3). The Ni concentration reached a constant level at 41-50 m altitude location (Fig. 8). This result suggests that soil near the main road is polluted by traffic activities. The change in available soil Ni concentration with an increase in altitude was described better by eqn. 2 at significant level than by eqn. 1 (Table-3). The EF value of soils Ni in present study ranged from 1.36 to 2.29 (Table-4) and increased towards motorway approch (Fig. 8). As we use the EF value around 1.5 as the critrial level to distinguish the pollution source from traffic activites to natural erosion and agricultural activities, it is found that the soils within 20 m altitude locations were strongly affected by traffic activities. This result provides further evidence to illustrate that the traffic activities are the main contributors to Ni pollution.

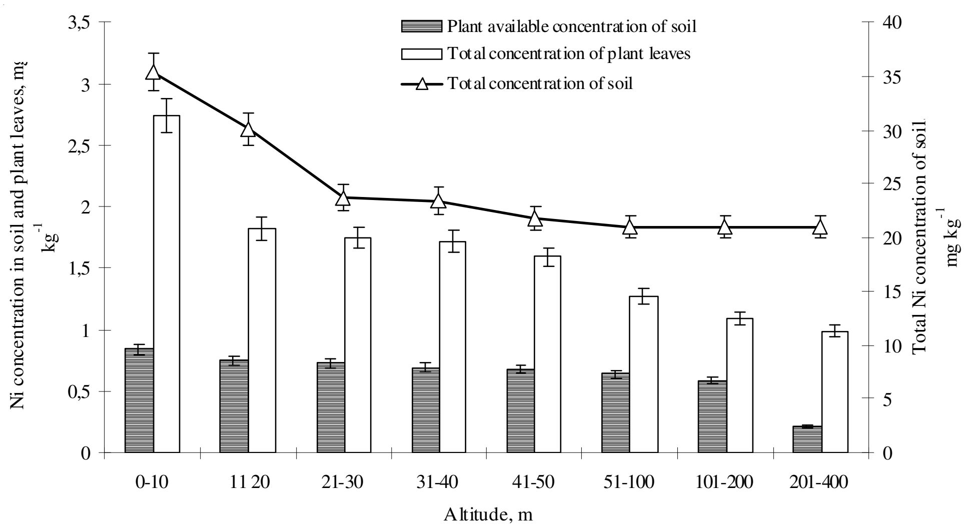

Fig. 8. Distribution of concentration of Ni in soil total and available forms and hazelnut leaves with location altitude

Lead: Lead is a trace element and is a potentially toxic metal to all organisms. It has been used in leaded petrol, diesel oil and also in unleaded petrol (< 0.015 g L^{-1}) and is an main pollutant from traffic activities[10,29,30,34,41-45]. The toxic trigger and action concentration was set at 500 and 813 mg kg^{-1} by ICRCL[35], while Efroymson *et al.*[37] and ERD[38], respectively set at 50 and 120 mg kg^{-1}. Netherland government set its target level[39] at 85 mg kg^{-1}. The concentration of total Pb in all present soil samples ranged between 94 and 680 mg kg^{-1}. This data shows that the Pb pollution is serious in this area, especially near to motorway. The pollution of Pb by fertilizers will be minor compared to atmospheric deposition[36]. The decrease in total soil Pb concenration with increase in atltitude is described better by eqn. 2 ($p < 0.01$) than by eqn. 1 (no significance) (Table-3). The concentration did not reach a constant level untill 101-200 m altitude (Fig. 9). The concentration of Pb in hazelnut leaves (Y_{PbL}), ranged from 0.96 to 1.53 mg kg^{-1}, is related linearly to soil total Pb concentration (X_{PbTS}): $Y_{PbL} = 0.879 + 0.00087\ X_{PbTS}$, $R^2 = 0.959$, $p < 0.001$. Usually the concentration of heavy metals in fruit was lower than in leaves. The EF factor of Pb ranged from 1.10 to 8.00 (Table-4) and increased towards the roadside (Fig. 9). This indicates that, traffic activities are the major contributors to Pb pollution and the drift of these emissions can reach 100 m altitude and seriously pollutes the soils within 50 m altitude area with EF value higher than 2[29].

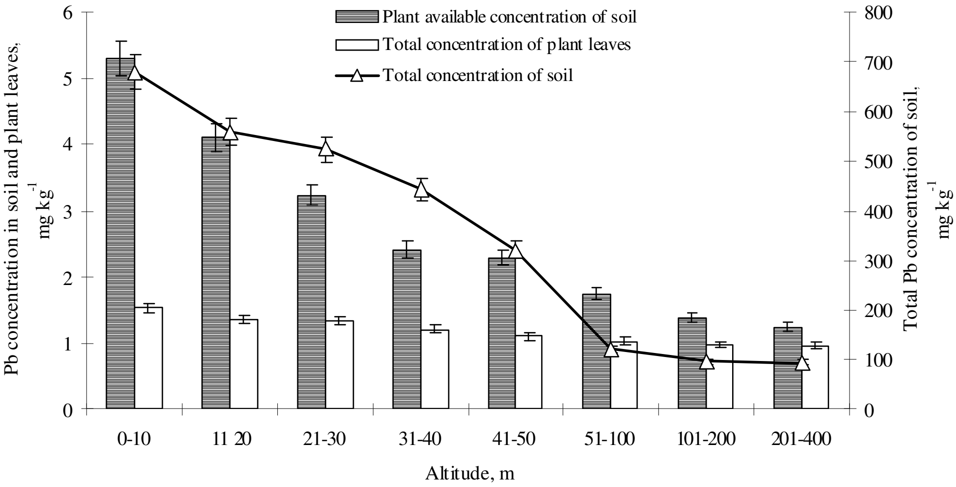

Fig. 9. Distribution of concentration of Pb in soil total and available forms and hazelnut leaves with location altitude

Zinc: Zinc is a common component in leaded petrol, diesel oil and even in unleaded petrol[30,41,43] and in tyre wear or brakes[34]. Inevitably, Zn is a pollutant from traffic activities on roadside soils[10,29,34,42,44,45]. The toxic trigger and action concentrations were set at 300 and 1665 mg kg^{-1}, respectively, by ICRCL[35], while Efroymson *et al.*[37] set at 50 mg kg^{-1} and the Netherland government set the target level[39] at 140 mg kg^{-1}. The concentration of total soil Zn in present study site ranged from 270 to 410 mg kg^{-1}. Thus the soil data shows that the study area has Zn pollution. However, the Zn concentration of the hazelnut leaves was lower than the data[25,40]. The concentration of Zn in hazelnut leaf (Y_{ZnL}) has no significant relation to soil available Zn and is related to soil total Zn (X_{ZnTS}) concentration only at siginificant level: $Y_{ZnL} = -14.3 + 0.106\ X_{ZnTS}$, $R^2 = 0.673$, $p < 0.05$. The pollution of Zn in arable lands was mainly from the fertilizers, especially from manure, the contribution of Zn from the atmospheric deposition was minor[36]. The total soil Zn concentration decreased with the increase in altitude and reached a constant level at 21-30 m location altitude. This result indicates that the pollution of source of Zn was mainly by farming activities and the only affected area due to traffic activitis was the land closer to main road within 30 m location altitude (Fig. 10). The decrease in total soil Zn concenration with increase in atltitude was better described by equation eqn. 1 ($p < 0.001$) than eqn. 2 ($p < 0.05$) (Table-3). The EF value of Zn ranged from 1.14 to 1.34 (Table-4) and increased with approach towards motorway (Fig. 10). This further provides strong evidence that the traffic activities were not the main contributors for the Zn pollution in this area. The total concentration of Zn recorded in the highest altitudal location was 351 mg kg^{-1} and the main traffic pollutant Pb could reach only 100 m altitude location. Hence it is beyond doubt that the main contibutor of Zn accumulation in soils in this area is farming activities.

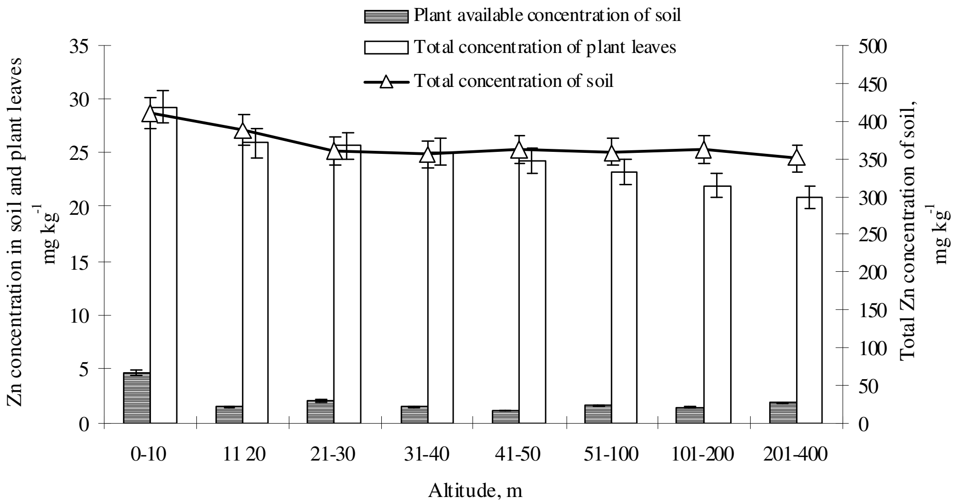

Fig. 10. Distribution of concentration of Zn in soil total and available forms and hazelnut leaves with location altitude

Conclusion

The results of this study show that the contamination of roadside soils with heavy metals from the traffic activities is not a common problem along the 010-17 motorway, except for Ni, Cd and Pb. But the accumulation extent of Ni was still at low level. The accumulation of all the studied elements was inevitable due to the erosion situation of this area. The source of Cu and Zn was mainly from farming activities. The EF values also indicate that the enrichment of these trace elements is not mainly from the traffic activities. For this area, at the critical EF value of 1.5, sources of pollutant namely, traffic activity to erosion and agricultural activities can be distinguished. Further studies should be conducted to trace the sources which cause the high accumulation of Cu and Zn in soils of the study area.

ACKNOWLEDGEMENT

The authors thank to Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey for their analysis support.

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(*Received*: 30 April 2008; *Accepted*: 14 March 2009) AJC-7340