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Determination and mapping of cadmium accumulation in plant leaves on the highway roadside, Turkey

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Abstract: This study investigates cadmium (Cd) accumulation in the plant leaves of juglans regia (walnut) and cydonia oblanga (quince) trees related to traffic emissions on the highway roadside. The plant leaf samples were collected from 20 sites on the D-100 Highway roadside and washed with deionized water before analyzed. Determination of Cd was carried out using an inductively-coupled plasma-mass spectrometer after microwave digestion of the samples. Cd concentration on the plant leaves was found to be between 0.04–0.11 mg/kg. In order to determine the traffic-based emissions, vehicles were counted and an emission inventory was prepared. 0.18 tons of Cd was found to be delivered into the atmosphere every day. Cd accumulation depends on traffic density because there were no residential area and industrial plants. The distribution of Cd accumulation caused by traffic emissions was mapped by using a geographic information system (GIS). The maps showed that the Cd accumulation was high in the areas near the highway and then gradually decreased by moving away from the highway.

Introduction

It is well known that the concentration of trace elements in soil, water and air continues to increase due to numerous variable factors, such as industrial activities, traffic emissions and domestic waste. Many trace elements are present in petrol, deisel oil and are emitted by vehicle exhaust. It is known that these trace elements have the potential to accumulate in plants, animals, other living organisms and soil. Even a minimal concentration of some trace element ions like cadmium (Cd), lead (Pb) and arsenic (As) is toxic to living organisms (Mendil and Tuzen 2011).

Trace elements accumulation in plants growing on roadsides is mainly due to heavy traffic on roads. The amount of accumulated metals depends on the density of the traffic, terrain structure (steep/gradient, flat), terrain area (junction, main road side, etc.), part of the plant (leaf, stem, fruit) and the direction of the wind. Sisman et al. (2002) found that the accumulation of metals is higher in steep areas than in flat areas.

A great proportion of Cd that reaches the plants and soil is due to the precipitation of Cd that is in the air in the form of little dust particles. More than 40% of the accumulated Cd in plants near industrial and heavy traffic areas comes from the air (EPA 1987, Sharma and Dubey 2005). It has been calculated that the annual amount of Cd particles precipitated in roadside soil in heavy traffic areas is 0.2–1 mg per m^2 (EPA 1987).

The effects of Cd on the environment and human health are well-known. Cd is nonessential trace element for plants when compared to other trace elements and it is 2–20 times more toxic than the others. More than 3 mg/kg of Cd has a toxic effect in soil, while more than 1 mg/kg is toxic to plants on a dry matter basis (Benavides et al. 2005). Cd mostly accumulates in the leaves of plants. Plants can take up Cd ions both metabolically as well as passively, and Cd ions can easily be transported within the plant. Especially organic substances can easily absorb Cd ions and so Cd can be found at high concentrations in the leaves and roots. In unpolluted areas, Cd levels in plants are in the range of 0.01 and 0.03 mg/kg.

There have been numerous studies investigating trace element accumulation in roadside plants that have generally focused on lead accumulation. Some of these woody and herbaceous plants include pine, oleaster, acacia, cypress, cedar, corn, oleander, grass and lettuce. As a result, the amount of lead accumulated is greater in dense traffic areas. Hence, there is a direct correlation between the lead accumulation, the density of the traffic and air circulation; as the distance from the highway increases, the amount of accumulated lead decreases (Yassoglou et al. 1987, Onasanya et al. 1993, Xiong 1997, Onianwa et al. 2002). In other studies, the accumulation of Cd, Cr, Fe, Mn, Cu, Ni, As, Sn, Ti and Zn elements in roadside woody and herbaceous plants was investigated and their concentrations were found to be higher than the normal level on the roadside and accumulation decreased away from the highway (Haktanır et al. 1995, Sawidis et al. 1995, Aksoy et al. 1997, Chronopoulos et al. 1997, Luilo et al. 2003, Staszewski et al. 2015). However, in these studies, emission inventories were not prepared for the explanation of trace element accumulation due to transportation vehicles. Also, the emission correlation analysis results were not mapped using GIS software.

The aim of this study was to investigate Cd accumulation in tree leaves in a dense traffic area on the D-100 main highway between Kocaeli and Sakarya in the northeast of Turkey. The leaves were collected and analyzed in the laboratory. The vehicle inventory was created and the distribution of Cd accumulation was mapped by using GIS software. Cd accumulation in plants as a result of exposure to vehicle emissions should be monitored due to the negative effects on human and environmental health.

Material and Method

Study field

The study field is located 29º57'–30º53'E longitude, 40º17'–41º13'N latitude, of the sea level. Throughout the study field the climatic characteristics of the Marmara and Black sea regions are apparent. The winter involves heavy rainfall and warm temperatures, while the summer is generally hot. The dominant are northeastern and northwestern winds. The study area is the roadside of the D-100 highway between the cities of Sakarya and Kocaeli where there is heavy traffic. This highway is generally used by intercity transport vehicles and TIR trucks. There are no residential areas, industrial plants or traffic lights close to the study area (Figure 1). There is considerable pollution from road traffic. Air pollution related to traffic is important in this study because the study area is located on the roadside covered by quince and walnut trees.

Sample selection and analysis

Quince and walnut trees have been cultivated as commercial agricultural activities in the study area. Quince and walnut trees were selected as samples because they are perennial plants and cover large area, being used in commercial areas (Wittig 1993).

The plant leaves were collected from D-100 highway, transferred to the laboratory and washed with deionized water. The leaf samples were collected randomly from 20 trees (10 walnut and 10 quince trees) as shown in Figure 1 and the sample point coordinates were identified with a Global Positioning System (GPS). The sampling was started at the edge of the highway and moved away step by step. 20 samples at least were taken from the sides of branches of each tree overlooking the road. The samples were collected from points between 50–500 m away from the highway.

As in many previous studies, the leaf samples were transferred to the laboratory and washed briefly and rinsed two times with deionized water in order to remove any dust and particles from the leaf surface (Onder et al. 2006, Karademir 1992, Kınalıoglu et al. 2009). All samples were dried at 80°C in oven (Nüve, model, Ankara, Turkey) for 24 hours, then ground using a porcelain mortar and stored in plastic bags.

In order to validate the determination method for Cd levels used in this study, a standard reference material tobacco leaf was utilized and certified and the obtained values were 1.52 and 1.46 mg/g, respectively. The recovery was calculated to be 96%. The found value corresponds well with the certified value and hence, the method could be used reliably for the determination of Cd levels in the leaf samples.

The Cd concentrations were determined using ICP-MS after digestion of the samples in a microwave digestion system. For this purpose, leaf samples (0.2 g) were weighed with a sensitivity of 0.1 mg and then dissolved in a microwave digestion system (Topwave, Analytik Jena AG, Jena, Germany) by adding 7 mL of HNO_3 (65%), 1 mL of H_2O_2(30%) and 0.5 mL of HF (40%). The final volume was completed with 50 mL of the obtained solution. In order to check the accuracy of the method, a certified reference material tobacco leaf

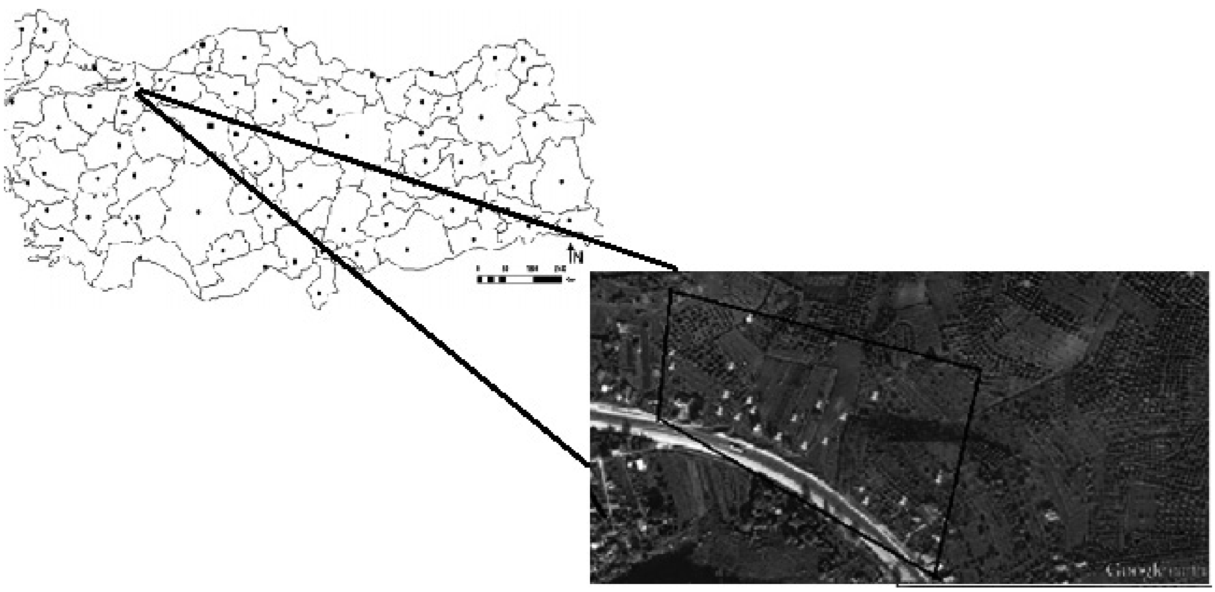

Fig. 1. Study area and points of sample collected

(Virginia Tobacco Leaves, CTA-VTL-2) was dissolved under the same conditions.

Cd concentration in the obtained solution was measured using an inductively-coupled plasma-mass spectrometer (ICP-MS, Agilent 7500cx; Agilent Technologies, CA, USA). The Cd concentration of the leaf samples and certified reference material tobacco leaf were calculated in mg/kg.

Preparation of the emissions inventory related to traffic

The vehicle emissions inventory was calculated and prepared for the observation of the contribution of traffic on the Cd accumulation in the studied area. The purpose of the emission inventories was to identify air pollutant sources and the amount of pollutants released into the atmosphere from these sources. In this way, more effective results and recommendations could be produced for air pollution control and air quality (Elbir et al. 2001).

In this study, only heavy vehicles were included in the assessment for the calculation of emission inventory. The engine of commercial vehicles takes more fuel and gives off more emissions with increased load amount. Moreover, in order to recognize vehicles using diesel oil more easily in vehicle counting, heavy vehicles using this kind of fuel were taken into account. Diesel oil is one of the important sources of Cd (Sanda 1993).

In the first part of the inventory study, vehicle counts were conducted in order to determine the intensity of the highway traffic. Vehicle counting was carried out over four different high traffic density hours during the day and vehicles were counted by two persons. The emission factor for Cd was taken from the 2009 EMEP/EEA mission inventory guidebook (Table 1).

Table 1. Emission factor for cadmium (EMEP/EEA 2010)

Category	Cadmium
Passenger cars, gasoline	0.01
Passenger cars, gasoline catalyst	0.01
Passenger cars, diesel	0.01
Passenger cars, LPG	0.0
LDVs, gasoline	0.01
LDVs, gasoline catalyst	0.01
LDVs, diesel	0.01
HDVs, gasoline	**0.01**
HDVs, diesel	**0.01**
Motorcycles < 50cm^3	0.01
Motorcycles > 50 cm^3	0.01

In order to move a vehicle, it has to have mechanical pulling power to support acceleration, uphill climbing, rolling resistance and wind resistance. The necessary power for acceleration and hill climbing is quite high compared to the others. Therefore, the region's elevation change and acceleration are important for fuel consumption and emissions. Vehicle emissions were calculated using Formulas 1 and 2.

$$\dot{W}_{Total\ power\ of\ vehicle} = \dot{W}_{slope} + \dot{W}_{acc.} + \dot{W}_{roll.} + \dot{W}_{wind} \quad (1)$$

$\dot{W}_{slope.}$ $(\dot{W}_{uphill}) = m.g.V.sin\Theta$
$\dot{W}_{acc.}$ $(\dot{W}_{accelaration}) = m.a.V$
$\dot{W}_{res.}$ $(\dot{W}_{rolling\ resistance}) = m.g.C_{roll.}V$
$\dot{W}_{wind.}$ $(\dot{W}_{wind\ resistance}) = 0{,}5\rho.A.Cd.(V+Vw)^2\ V$

$$\dot{W}_{total\ power\ of\ vehicle} = m_{fuel}\ x\ \eta_{vehicle}\ x\ Q_{LHV} \quad (2)$$

- Weight (m): Vehicles have been accepted full and an average of 16 tons was calculated.
- Acceleration of gravity (g): is accepted to be an average of 9.81 m/s^2
- Density(ρ): the air density is 1,293 kg/m^3
- Acceleration (a): Heavy vehicles are taken as the average of 2 m/s^2
- Slope angle (Θ): the region is close 0 so angle of inclination is regarded as 0.
- The car front projection area (A): A = 0.9. width (4). height (2) = 7.
- Average speed (V) : vehicles have been accepted with a full 75 km/h
- Wind speed (Vw): According to the meteorology 2 m/sec
- Wind resistance coefficient (Cd): is accepted as 0.3.
- Rolling resistance coefficient (C_{roll}): is accepted as 0.01 (EMEP 2009)
- Efficiency: the average thermal efficiency of the internal combustion engine 30%
- Minimum heating value of fuel: is taken as 40000 kJ/kg (EMEP 2009)

The daily amount of accumulated trace elements was found by dividing the total amount of fuel by the emission factor using Formulas 1 and 2.

Mapping of accumulation distribution

The accumulation data were transferred to the GIS database and accumulation distribution was mapped using GIS software. In order to show the spatial distribution of Cd the accumulation maps were created using spatial interpolation methods. The results of the analysis were loaded into the Surfer program and maps were prepared by using the Kriging method. The Surfer software is a type of Geographic Information System software for spatial analysis and the Kriging Method (Golden Software 2002). Satellite images taken from Google Earth were used as base maps.

Results and discussion

Cd levels in leaves

Cd concentrations in the leaves of walnut and quince are shown in Table 2. The Cd concentration in leaves ranged from 0.04 to 0.11 mg/kg. It should also be noted that Cd concentration exceeded the limit value in all samples (The limit is 0.01–0.03 mg/kg in unpolluted areas). Therefore, it can be said that washing procedure is not important for removing trace element in suburban area (Caselles et al. 2002).

It was observed that Cd accumulation is at the maximum level in inclined areas and in the areas which are closest to the highway.

Cd accumulation differences between quince and walnut leaves were ignored due to structural features of leaves and were not considered.

Results of emission inventory

In order to determine the daily average vehicle number, the vehicles moving on the highway were counted and then categorized as a small truck, heavy vehicle, automobile or motorcycle. The obtained results given in Table 3 show that the number of total vehicles was 19,860 per day and the percent ratio of heavy vehicles (3,786) to total vehicles was 19%. Emissions were calculated using EMEP/EEA emission factors in formulas 1 and 2 (Table 3).

Total power of vehicle was calculated as 669,12 kW (Formula 1). By using this result, m_{fuel} was calculated with formula 2 and the result was 0.0558 $kg \cdot day^{-1}$. When this result was multiplied by the number of heavy vehicles, the result was 18,239,795 $kg \cdot day^{-1}$. As a result, the total fuel amount was calculated with EPA emission factor and it was determined that there were 0.18 tons of Cd ion emitted to the atmosphere daily and therefore, the emitted Cd could accumulate in the leaves of the trees. When it is considered that there are no residential areas or industrial plants around the study field, it is clear that the pollution was caused by traffic. As mentioned before, more than 40% of the accumulated Cd in plants near industrial and heavy traffic areas comes from the air. Because of that, the emission inventory is important in terms of emphasizing that the Cd accumulation was related to traffic.

Demonstration of accumulation distribution by GIS

The topographical structure of the study field was shown according to the coordinates at sample points (Figure 2). In the studies on trace elements, the topographical properties of fields from where plant samples are taken influence the amount of trace element in plants. While the amounts of trace element obtained from fields at an incline have higher values, when the study field is flat, low accumulation values are observed. In this study it is seen that the height values increased towards the north, east and west directions in the topography.

The accumulation level map prepared with the results of sample analyses is shown in Figure 3. The points of maximum Cd accumulation were observed at points no 1, 3, 12 and 13 (Table 2). The map shows that the maximum level of Cd accumulation was at the nearest point to the highway in the study areas. Obviously the amount of accumulation decreased by moving away from the highway. This fact shows that Cd accumulation is the result of exhaust emissions. There is no residential area nor an industrial plant in the study area and in its surroundings, hence Cd accumulation is related to traffic emission only. Besides, farmers use minimum amount of fertilizer according to Sakarya directorate of provincial agriculture database. The obtained results are in good agreement with previous studies reported in the literature (Maisto et al. 2004, Akyol and Öztürk 1997). GIS plays a complementary role in the presentation of accumulation and pollution distribution and also supports the decision-making process (Macit and Gümrükçüoglu 2012).

Conclusion

The levels of Cd found in the leaves were higher than acceptable levels. The emission inventory results indicated that the roadside Cd pollution was highly positively correlated with traffic density. The maximum level of Cd accumulation was observed in the points near the highway and decreased relative

Table 2. Cd accumulation on washed samples

Sample	Tree	Cd mg/kg	Sample	Tree	Cd mg/kg
1A	Quince	0,09429	11A	Quince	0,07006
2A	Walnut	0,05676	12A	Walnut	0,10165
3A	Quince	0,09391	13A	Quince	0,10592
4A	Walnut	0,04724	14A	Walnut	0,05682
5A	Quince	0,05313	15A	Quince	0,06794
6A	Quince	0,07027	16A	Quince	0,07122
7A	Quince	0,06349	17A	Quince	0,06257
8A	Walnut	0,05164	18A	Walnut	0,05093
9A	Quince	0,085	19A	Quince	0,07655
10A	Walnut	0,07931	20A	Walnut	0,07239

Table 3. Average daily vehicle number

	Vehicle number according to hours				Daily average vehicle number
	08.00– 09.00	12.00–13.00	15.00–16.00	19.00–20.00	
Small truck	122	148	132	159	3366
Heavy vehicle	158	142	135	196	3786
Automobile	586	475	542	496	12 594
Motorcycle	3	5	3	8	114

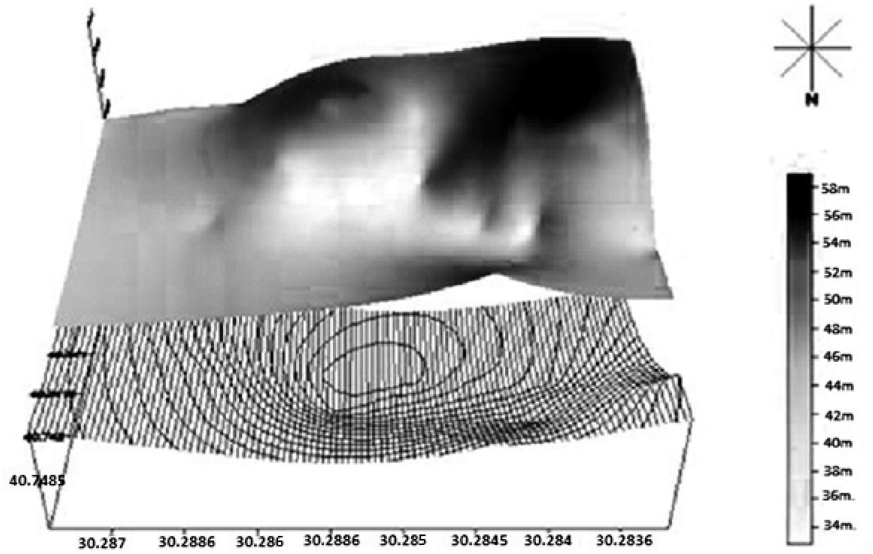

Fig. 2. Topographic structure on study area

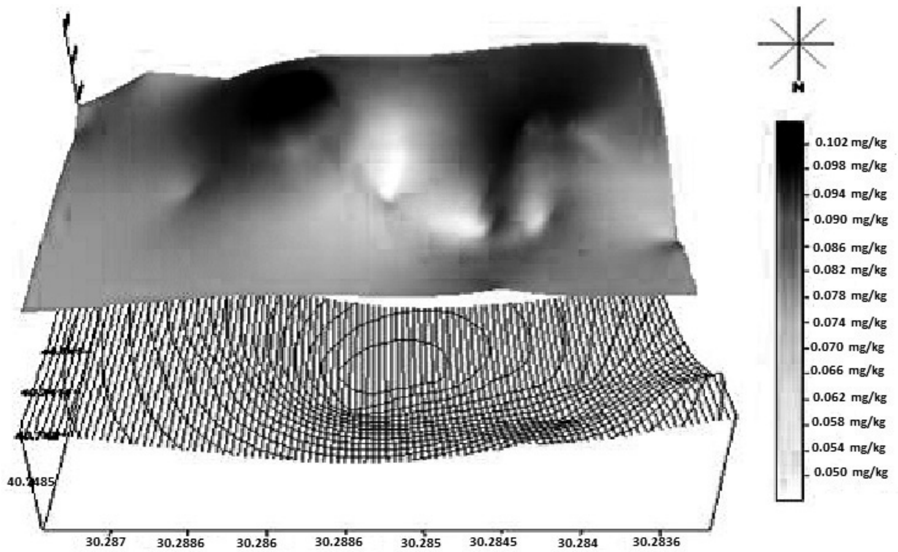

Fig. 3. Distribution of Cd accumulation

to the distance from the highway. Cd is a toxic element, so analysis of accumulation and plotting the distribution on GIS maps are important and provide invaluable information for decision makers.

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