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SPATIO-TEMPORAL VARIATION IN CADMIUM RELEASED BY AUTOMOBILES ALONG TWO ROADS IN PAKISTAN

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Abstract

Cadmium (Cd) is a highly toxic metal in the environment. Automobiles release a considerable amount of Cd along roads. In this study, we assessed the level of Cd in five herbaceous plant species (*Calotropis procera, Datura alba, Ricinus communis, Parthenium hysterophorus* and *Cenchrus ciliaris*) commonly growing along two roads i.e. Motorway (M-2) and Faisalabad-Sargodha road (FSR) in the Punjab, Pakistan. Plant and soil samples were collected in all the four seasons from roadsides. Samples taken 100 m away from roads were designated as control. Cd was analyzed in all the plants and soil samples by Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES). Spatial and temporal variation of Cd concentrations both in plants and soils was clearly seen in results. With compared to control ones, plants and soils showed higher concentration of Cd along roads. The highest contamination of Cd was recorded during summer, whilst, the least was noticed during winter. Among plants, *Calotropis procera* leaves accumulated the highest level of Cd which proved as bioindicator of Cd. The Cd concentrations in plants along roadsides positively correlated with traffic density. So, control measures are required to overcome transport sector related pollution which may become severe in forthcoming days.

Key words: Cadmium, Bioindicator, Metal, Pollution.

Introduction

The increased anthropogenic activities e.g. industrial processes, fossil fuel combustions and traffic emissions are adding surplus amount of pollutants into the atmosphere (Li *et al*., 2001; Bhatti *et al.*, 2017). The municipal environments contain an intricate mixture of air born pollutants, but the dominating feature of urban air is road traffic emissions, which are significant and increasing source of pollution at the global level (Kammarbauer & Dick, 2000; Colvile *et al*., 2001; Kadi, 2009; Wei & Yang, 2010; Nikula *et al*., 2011; Khalid *et al.*, 2017a). The concentrations of heavy metals are continually increasing in air, water and soils.

Among metals, cadmium (Cd) is very toxic and adversely affects plants, animals and humans (Daud *et al*., 2013; Aziz *et al.*, 2014). It has been classified as principle human carcinogen (Anon., 2011; Anon., 2012; Luckett *et al*., 2012). Vehicular exhausts are the main source of Cd in areas adjacent to roads (Amusan *et al.*, 2003; Faiz *et al*., 2009; Pirzada *et al*., 2009). It comes from lubricant oils and tire abrasion (Weckwerth, 2001; Ozaki *et al.*, 2004). In the last few decades, yearly global release of Cd by various sources has attained 22,000 tons (Singh *et al*., 2003). The bioavailability of metals and their effects depend on different factors, i.e., environmental conditions, organic matter in soil, pH, fertilizers and plant species (Cheng, 2003). The concentration of metals also depends upon seasonal and spatial variations (Sarasiab, 2014; Johansson *et al.*, 2007). Metals are usually found in higher concentrations during warmer periods of the year due to high temperature (Papafilippaki *et al.*, 2007; Iwashita & Shimamura, 2003). Davis & Birch (2011) found spatial variation of Pb, Zn and Cu concentrations along roadsides in Sydney, Australia. While, they found no temporal variation of these metals.

Cd decreases seed germination (Abraham *et al.*, 2013), interferes chlorophyll biosynthesis (Vassilev *et al.*, 2005), disrupts activity of many enzymes, e.g. catalase, peroxidase, glutathione synthase, ascorbate peroxidase (Vassilev *et al.*, 2002), reduces transpiration, reduces or inhibits growth (Mendelssohn *et al*., 2001) and causes DNA fragmentation in plants (Baudouin *et al.*, 2002). The increase in metals deposition from motor vehicle emissions has raised the concerns about food quality risks and human health. Metals emitted by vehicles can easily get deposited on roadside soil and vegetation, grazed on by animals and enter food chain (Ayodele &Oluyomi, 2011).

Biomonitoring is a way to find out the hazardous effects of environmental pollution over a fretful region (Khan& Sadiq, 2005). Some plant species accumulate excessive heavy metal concentrations in different parts especially in leaves and prove very good bio indicators of metals pollutants in the environment (Turan *et al*., 2011). They that can be used to assess the level of toxicity in area (Wagh *et al*., 2006; Ramadan, 2003). Earlier researches have recognized some plant species which proved to be good bio indicators of metals e.g. *Dalbergia sissoo* (Naveed *et al*., 2010), *Fraxinus excelsior* L. (Aksoye & Demirezen, 2005), *Calotropis procera* (Singh *et al.*, 1995), *Nerium oleander* (Espinosa & Oliva, 2006; Oliva & Espinosa, 2007) and *Parthenium hysterophorus* (Khalid *et al.*, 2017b). In this study we have chosen five wild plant species for monitoring the level of Cd in soil along roads under study. *Datura alba*, *Ricinus communis,* and *Calotropis procera* are shrubs. *Parthenium hysterophorus* is a perennialherb and *Cenchrus ciliaris* is a grass. *Parthenium hysterophorus* is exotic plant species, while others are native to this region.

Punjab is the most populated province of the Pakistan with high traffic density. Faisalabad and Sargodha, two divisional headquarters are directly interconnected by a metallic road (FSR) having a number of residential settlements along it. Crushed stone is supplied all over the Punjab by heavy duty trucks through this road for the construction of buildings, however the metal pollution along it has not been examined. The second road, Motorway-2 (Pindi Bhattian to Lillah) also has special ecology. The traffic load comprises of cars, air-conditioned buses, vans, mini buses and small trucks. This road passing through cultivated fields and wild lands has not been monitored yet. Therefore, the study was accomplished to assess Cd pollution in vegetation caused by automobiles along two roads i.e., Faisalabad to Sargodha (FSR) and Pindi Bhattian to Lillah (M-2) with objective to find out spatial and temporal variation in Cd along these roads and to explore some good bio monitors for Cd.

Materials and Methods

To examine Cd pollution caused by automobiles, we selected two roads [Faisalabad to Sargodha road (FSR) and a section of Motorway (M-2), Pindi Bhattian to Lillah] in Pakistan (Fig. 1). Five sites at almost uniform distance were selected on each of two roads. Three leaves of five most common plant species *Datura alba* L. (Datura), *Calotropis procera* L.(Ak), *Parthenium hysterophorus* L. (Gajarbuti), *Ricinus communis* L.(Arund) and *Cenchrus ciliaris* L. (Anjan grass) growing along both roads were collected. The survey was conducted in all the four seasons of the year for the required sampling and data collection. The average temperature in study area during day time in summer, autumn, winter and spring was 40.1°C, 35.5°C, 12.5°C and 27.5°C, respectively. It was not possible to collect all the plants at all sites during winter and autumn. Three soil samples from each site were also collected (0-10 cm depth). Plant and soil samples collected 100 m away from road were designated as control. All the samples were packed in plastic sealed bags, labelled, immediately placed in iced cooler and brought into the laboratory. Plant and soil samples dried in an oven following the method of Pandey *et al*., (2009) and digested for determining their Cd concentrations according to the methods of US - EPA (1996). For determining Cd contents, Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) Thermoi CAP 6300 model (Materials Research Laboratories, University of California Santa Barbara, USA) was used. The optimum working range of ICP-AES for measurement of elements ranged from 50 PPB to 100 PPM by weight. Calibration was done by standard solutions of high purity standards. Fuel (Petrol & Diesel) samples obtained from petrol stations (PSO and Shell Helix), located along roads under study were digested according to the method of Akpoveta & Osakwe (2014). Soot samples were also collected from exhaust pipes of vehicles running on roads under study and digested by following Atiku *et al*., (2011). Cd was then analyzed both in fuel and soot samples by atomic absorption spectrophotometer (Hitachi, Z-8200, Japan). Traffic density (number of vehicles per day) was noted at each study site along M-2 and FSR on specified days (midweeks and weekends) for two hours.

COSTAT (Cohort software, Berkeley California, USA) was used to analyze data using three way and two way analysis of variance (ANOVA). The Canonical correspondence analysis (CCA) technique was applied to data using Canoco computer package (Version 4.5) for windows to see spatial and temporal variation in data.

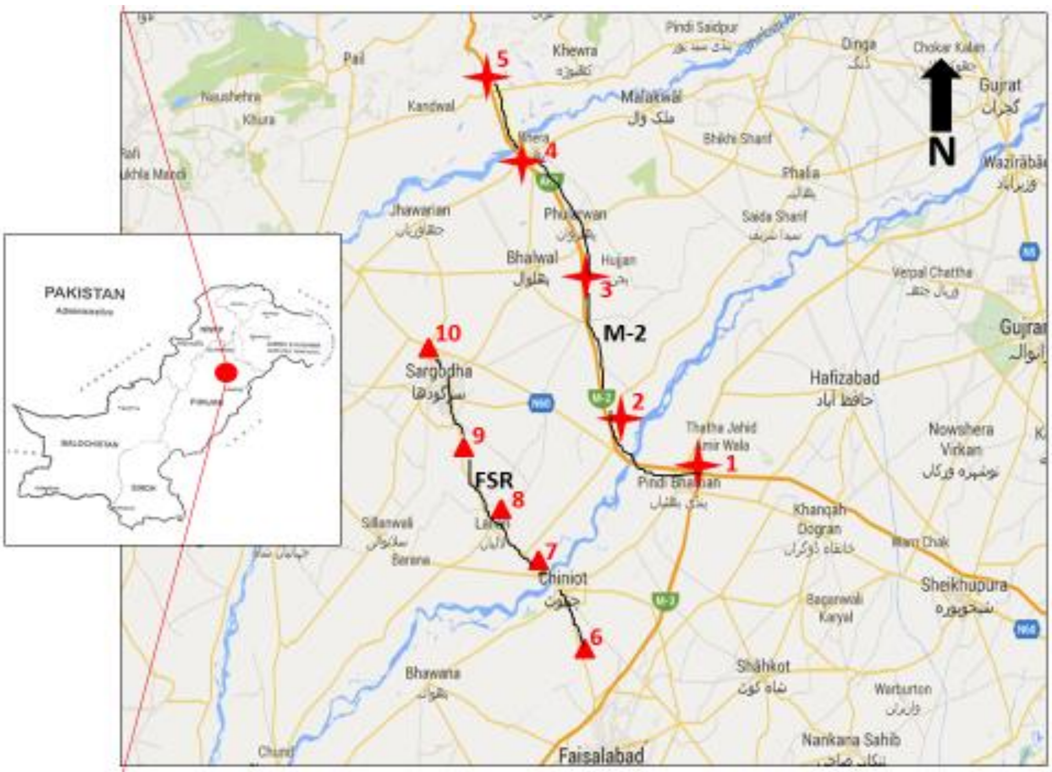

Fig. 1. Map showing sites on M-2 and FSR; where, 1. PindiBhatian, 2. Kot Momin, 3. Salim, 4. Bhera, 5. Lillah, 6. Pull Dingro, 7. Chiniot, 8. Chenab Nagar, 9. Ada-46, 10. Pull-111. (Picture is taken from Google Maps).

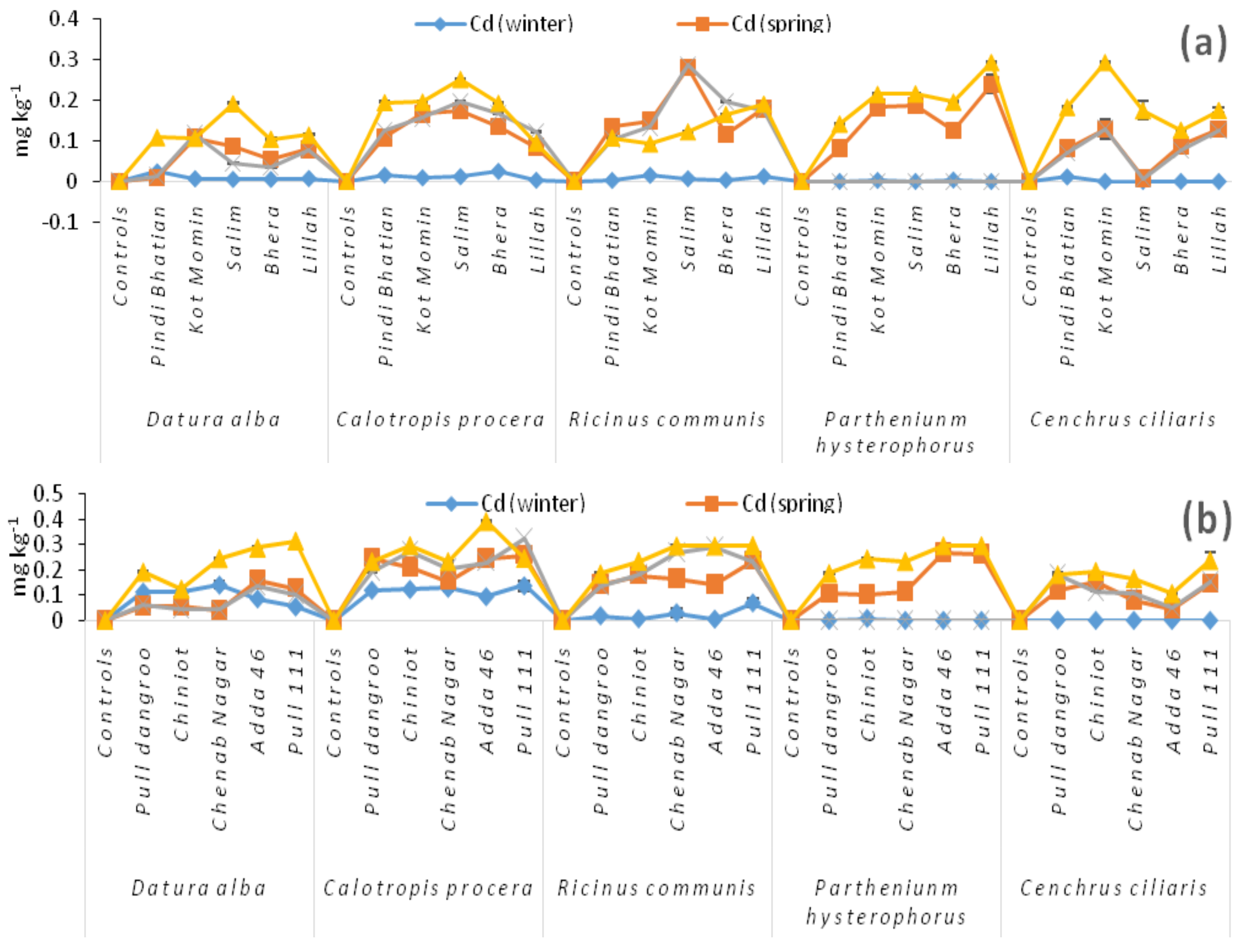

Fig. 2. The concentrations of Cd (mg kg^{-1}) in plants at various sites along M-2 (a) and FSR (b) in four seasons.

Results and Discussions

Plants: Plants collected from roadsides showed a marked contamination ($p<0.001$) of Cd as compared to their controls (Fig. 2a & b). *Calotropis procera* at Ada-46 on FSR accumulated the maximum concentration of Cd (0.392 mg kg^{-1}) during summer as compared to control followed by the concentration of Cd in *C. procera* during autumn at Pull-111 on FSR. *Datura alba*, *Ricinus communis* and *Parthenium hysterophorus* at Pull-111 showed significant ($p<0.001$) contamination of Cd during summer. At M-2 *P.hysterophorus* and *Cenchrusciliaris* accumulated the main concentration of Cd (0.294 mg kg^{-1}) at Lillah and Kot Momin respectively during summer. Among the four seasons, all the plants showed lowest concentration of Cd at all the sites during winter. The concentration of Cd varied from 0.002-0.392 mg kg^{-1} in plants. These findings are in conformity with the older studies (Swaileh *et al.*, 2001; Nawazish *et al.*, 2012). The observed contamination of Cd in some samples were above permissible limits (0.02 $mgkg^{-1}$) for plants (Anon., 1996). This metal is non-biodegradable and in humans its over exposure leads to bioaccumulation and it is also a cause of serious environmental deterioration (Su *et al.*, 2014). Kidneys may accumulate high concentration of Cd after long term exposure (Moon *et al.*, 1999; Borjesson *et al.*, 2000). Plants easily uptake Cd from roadside soils as compared to Zn, Pb, and Cu (Shahid *et al.*, 2017). Shafiq *et al.*, (2011) also reported a high level of Cd metal (2.96 mg kg^{-1}) in plant leaves along busy roads in Karachi. This Cd in roadside plants comes from wear of automobile tires due to the friction between surfaces (Weckwerth, 2001; Ozaki *et al.*, 2004). On the other hand, another group of scientists reported comparatively low (0.06 mg kg^{-1}) Cd concentration in leaves of wild plants in the vicinity of a highway in France (Viard *et al.,* 2004).

Canonical correspondence analysis (CCA) biplot showed significant variation of Cd concentration in plant species within different sites during different seasons (Fig. 4) along Motorway (M-2). During winter, *C. ciliaris* and *R. communis* showed their highest Cd concentrations at PindiBhattian and Kot Momin respectively. Similarly, highest Cd concentration in *C. procera* was found at Bhera, but Cd concentration in *P. hysterophorus* and *D. alba* did not show any strong association with any site (Fig. 4a). The highest concentration of Cd in *C. ciliaris* was found at Kot Momin during summer along M-2 (Fig. 4b), whereas, the concentrations of Cd in *P. hysterophorus* and *D. alba* were associated with Lillah and Salim respectively during summer. *R. communis* was weakly associated with Bhera for Cd concentration during summer along M-2. During spring and autumn, Cd contents in plant species did not show any strong association with sites along M-2 (Fig. 4c & d).

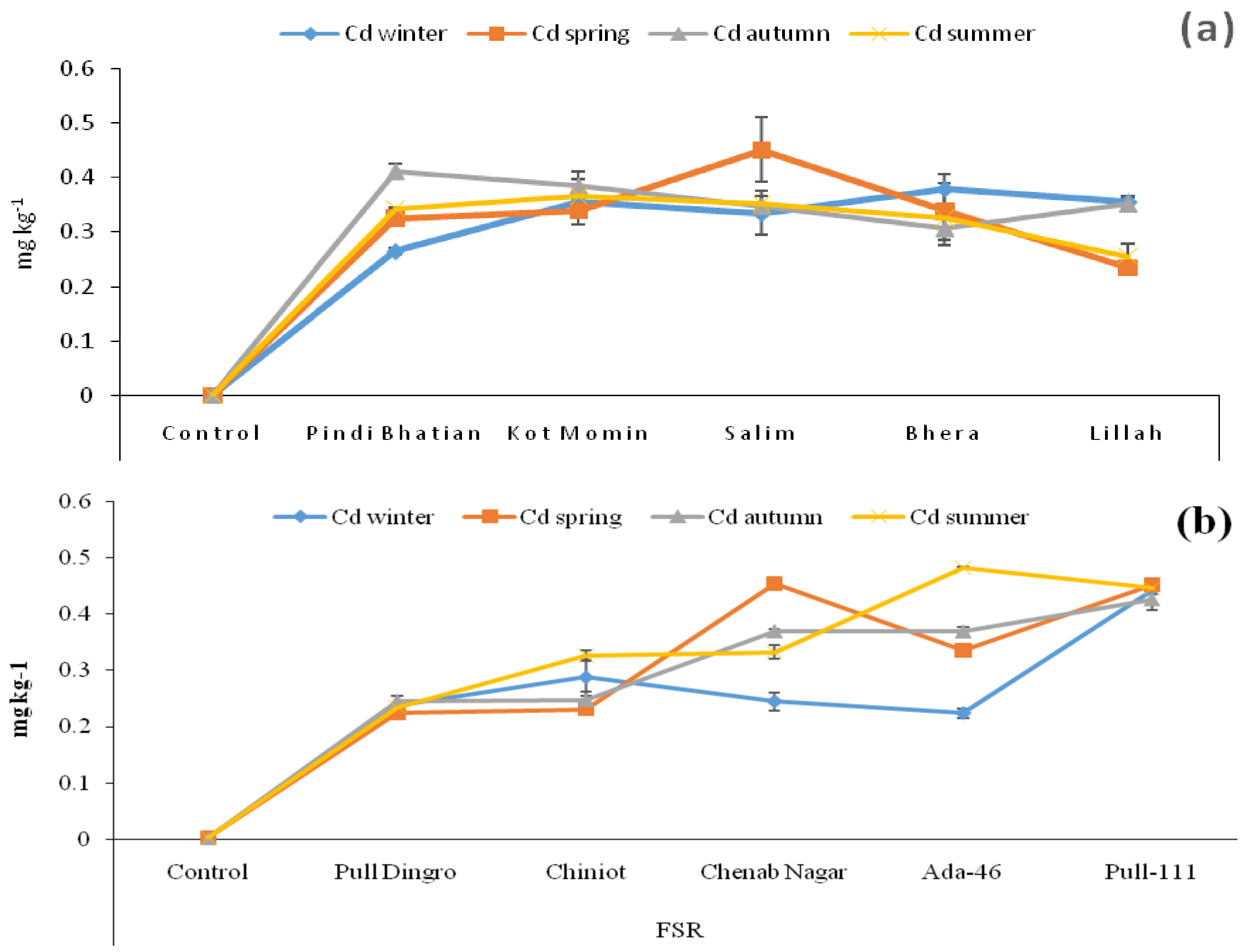

Fig. 3. The concentrations of Cd (mg kg^{-1}) in soils at various sites along M-2 (a) and FSR (b) in four seasons.

At Faisalabad-Sargodha Road (FSR), *R. communis* showed highest Cd concentration at Pull-111 during winter (Fig. 5a.). The highest Cd concentrations in *D. alba* and *R. communis* were seen at Adda-46 and Chenab Nagar respectively during spring (Fig. 5c). Cd concentration in *P. hysterophorus* and *C. ciliaris* did not show association with any site during spring (Fig. 5c). Similarly, during autumn, no association was found between Cd concentration in plant species and sites (Fig. 5d).

A significant spatial and temporal variation was noticed in the concentrations of Cd during different seasons. Cd was found in higher concentrations during summer. This might be due to the excessive wear and tear of tyres during high temperature and high traffic density. These findings are in consistent with previous findings (Harmens, 2007). Spatial distribution of Cd along roads depends upon traffic volume, road proximity, differential land use (Davis & Birch, 2011), vehicle emissions and point sources (Karim *et al.*, 2014). Baycu *et al.*, (2006) collected leaves of some tree species during spring and autumn from some urban areas in Istanbul. They found temporal variation in concentrations of Cd, Pb, Zn and Ni metals in two seasons as compared to control.

Soil: Soil samples collected from roadsides along both roads showed significant ($p<0.01$) contamination as compared to their controls. Soil taken from Salim during spring showed the maximum contamination of Cd (0.45 mg kg^{-1}) as compared to control on M-2 followed by the concentration of Cd at Pindi Bhatian in autumn (Fig. 3a). This increase in Cd might be due to high speed of vehicles at Salim and frequent use of brakes at Pindi Bhattian. The level of Cd in soil (0.352 mg kg^{-1}) was same during autumn and winter at Lillah on M-2. In case of soil taken from FSR, maximum concentration of Cd was noted during summer at Ada-46, might be due to high temperature (Fig. 3b). A slight temporal variation was found in Cd concentration at Pull Dingro and Pull-111 on FSR. While, strong temporal variation was noted at Chiniot, Chenab Nagar and Ada-46. Maximum concentration of Cd was noticed during summer (0.482 mg kg^{-1}) as compared to control, while, lowest concentration was noted during winter (0.223 mg kg^{-1}). Spatial variation was also found and significantly ($p<0.05$) correlated with traffic density. The degree of contamination depends upon traffic volume and brake use frequency (Kabadayi & Cesur, 2010). Degree of metal contamination is also related to high speed of vehicles (Duong & Lee, 2011). Kabadayi & Cesur (2010) found a range of Cd concentrations (0.02-6.16 $mgkg^{-1}$) in roadside dusts of Samsun city. The levels of Cd in roadside soils of

Beijing was much higher and decreased in concentration gradually with increasing distance from road (Chen *et al.*, 2010). Backstrom *et al.*, (2004) reported a temporal variation of Cd in roadside soils of Sweden. In another study conducted in Islamabad, Pakistan, Faiz *et al.*, (2009) found a much higher concentration of Cd (5 mg kg^{-1}) in their dust and soil samples collected from some busy roads. Spatial variation of Cd was also noticed by Wei *et al.*, (2009) in dust samples collected from 169 urban roadsides in China and it was related with traffic density.

Traffic density: The concentrations of Cd both in plants and soils were significantly ($p< 0.05$) positively correlated with traffic density (Table 1). These findings are in consistence with many other studies. Vehicles are the main source of Cd along roadside environments and its concentration depends upon traffic volume (Ozaki *et al.*, 2002). Our results are similar to the findings of Deepalakshami *et al.*, (2014) who also found the concentrations of Cd, Pb, Zn and Cu in vegetation along some highways positively correlated with density of traffic. Likewise, Cd metal in dust, soil and plants in many other studies have been presented to show the positive correlation with traffic volume (Madrid *et al.*, 2002; Nabulo *et al.*, 2006).

Fuel and soot: Soot can contribute to heavy metal pollution in the environment (Atiku *et al.*, 2011a). The concentration of Cd in petrol and diesel was 0.01 mg kg^{-1} and Cd concentration of soot was 0.5 mg kg^{-1}, which are lower values as compared to Atiku *et al.*, (2011), who reported comparatively higher Cd concentrations in raw gasoline (10.708 mg kg^{-1}), raw diesel (3.316 mg kg^{-1}) and soot (2.852 mg kg^{-1}) in Nigeria. According to Okorie *et al.*, (2010) the average concentration of Cd in soot was 0.396 mg kg^{-1} which is above permissible level for air and water devised by World Health Organization.

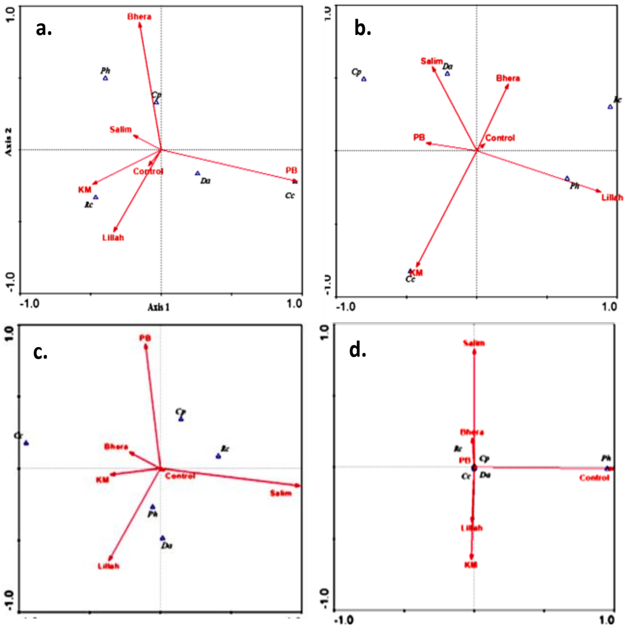

Fig. 4. CCA biplot for Cd concentrations in plant species at Motorway (M-2) a. Winter, b. Summer, c. Spring and d. Autumn. Plant species are abbreviated as *Da: Datura alba; Cp: Calotropis procera; Rc: Ricinus communis; Ph: Parthenium hysterophorus; Cc: Cenchrus ciliaris.* Sites are abbreviated as PB: Pindi Bhatian; KM: Kot Momin

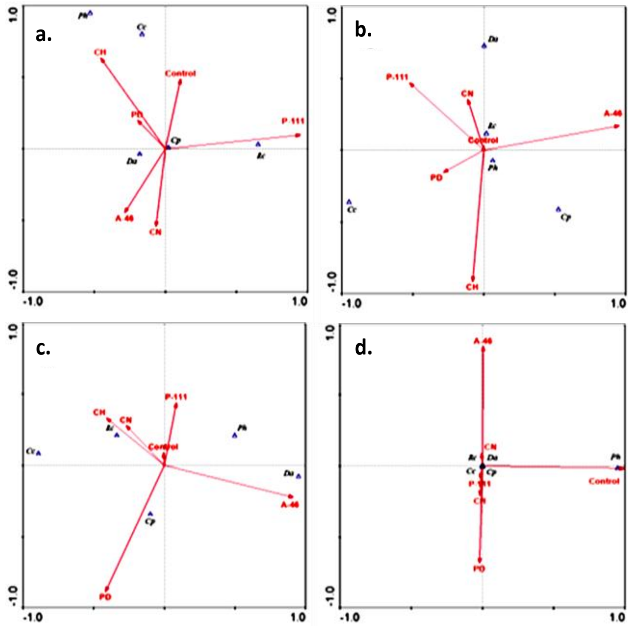

Fig. 5. CCA biplot for Cd concentrations in plant species at Faisalabad-Sargodha Road (FSR) a. Winter, b. Summer, c. Spring and d. Autumn. Plant species are abbreviated as *Da: Datura alba; Cp: Calotropis procera; Rc: Ricinus communis; Ph: Parthenium hysterophorus; Cc: Cenchrus ciliaris.* Sites are abbreviated as PD: Pull Dingro; A-46: Ada-46; CH: Chiniot; CN: Chenab Nagar; P-111: Pull-111.

Table 1. Pearson's correlation coefficient between traffic density and Cd concentration in plants and soils in all the four seasons on M-2 and FSR.

	M-2				FSR			
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
D. alba	0.706*	0.8445**	0.711*	0.922***	0.722*	0.7653*	0.532ns	0.8654**
C. procera	0.9021***	0.8211**	0.8843**	0.881**	0.832**	0.7743*	0.8732**	0.7765*
R. communis	0.7281*	0.8009**	0.8211**	0.657ns	0.711*	0.8253**	0.7114*	0.8876**
P. hysterophorus	0.9141***	0	0.722*	0.7764*	0.9266***	0	0.332ns	0.776*
C. ciliaris	0.8065**	0.678ns	0.771*	0.8211**	0.745*	0.7721*	0.7165*	0.7656*
Soil	0.865**	0.743*	0.773*	0.453ns	0.763*	0.882**	0.926***	0.825**

*** = $p<0.001$; ** = $p<0.01$; * = $p<0.05$; ns = Non-significant

Conclusions

The level of Cd metal was assessed in plants, soils, fuel and soot samples along M-2 and FSR. Cd concentrations were always higher in plants and soils as compared to control. In most of the plants and soil samples, the level of Cd is above permissible limits devised by WHO. The level of Cd in plants and soil showed a significant correlation with traffic density on both roads. Lowest Cd contamination was found during winter, while, maximum Cd values were obtained during summer in all the plant and most of the soil samples. Hence, the release of Cd depends upon temperature. Spatial and temporal trend for Cd was noticed along both roads depending upon traffic density, road proximity, temperature and other environmental factors. Cd was also found in fuel and soot. *Calotropis procera* accumulated the highest level of Cd, so it can be used for biomonitoring studies of Cd. Cd releases from vehicular emissions and result in the contamination of roadside environments causing toxicity. There is a need to regulate environmental conditions of the area under present study.

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