

Full Length Research Paper

The assessment of lichens as bioindicator of heavy metal pollution from motor vehicles activities

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The contamination of heavy metals released by traffic activities on roadside soils and crops are important problems in developed and developing countries for decades. An assessment of the extent of pollution in roadside soils is a key procedure to protect their ecological function and sustainable agriculture. The objectives of this study were to determine heavy metal contamination of roadside soils that originated from motor vehicles through the use of eight different lichens species situated along D-950 motorway in Erzurum. The results showed that the contamination of Pb, Cr, Cu, Cd, and Ni in roadside soils stemmed mainly from traffic activities, especially for Pb and Cd in this study area judging by their distribution patterns and their enrichment factors. Some of the lichen species such as *Xanthoria candelaria* (L.) Th. Fr., *Lecanora muralis* (Schreb.) Rabenh. and *Xanthoria elegans* (Link) Th. Fr., present in the region can be used to monitor pollution of traffic origin and *X. candelaria*, in particular, is a very good indicator of pollution of traffic origin. This kind of lichen could be an easy and cost-effective means of air pollution monitoring.

Key words: Bioindicator, enrichment factor, heavy metal pollution, lichen, traffic pollution.

INTRODUCTION

Soils of several regions of the world have been subjected and will also be subjected in the future to fertilizer and pesticide application, industrial and municipal pollution and industrial and residual elements arising from roadside. All these activities affect both chemical and physical soil properties, which will lead to changes in the behavior of trace elements in soils. Trace metal uptake by vegetation has already become serious environmental and health problem (Kabata-Pendias, 1995).

Contamination of roadside soils with heavy metals arises from various sources such as vehicles, road wear, and slipperiness control industries. Trace metal concentrations, such as Cd, Cu, Zn, and particularly Pb in surface soils have been the focus of many investigations.

Accumulation of these metals in surface soil is greatly influenced by traffic volume and motor vehicles, which introduce a number of toxic metals into the atmosphere (Lonati et al., 2006; Çiçek et al., 2008).

The bioavailability and environmental mobility of metals depend mainly on their existing form in soils. Pollutants that emit from automobiles are very diverse. Fossil fuel contains many kinds of heavy metals that will be emitted to the environment inevitably during combustion. The wear of auto tires, degradation of parts and greases, peeling paint and metals in catalysts are also suspected as sources of heavy metal pollution (Pecheyran et al., 2000). It is well known that automobiles are not only responsible for previous known forms of heavy metals pollution (Cu, Zn, and Pb), but also for the many other elements.

Lichens are an outstandingly successful group of symbiotic organisms exploiting a wide range of habitats throughout the world (about 20,000 species). Lichens

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Table 1. Mean (n = 10) and ranges for the descriptive parameters of 10 soil samples (0 -10 cm depth) from 0 and 100 m from road site.

Parameter	Unpolluted area (>100 m) Mean (mg kg ⁻¹)	Range (mg kg ⁻¹)	Polluted area (0 - 100 m) Mean (mg kg ⁻¹)	Range (mg kg ⁻¹)
Fe	12914	10205 - 13420	17667	12945 - 19445
Mn	299	255 - 420	426	266 - 530
Zn	31	23 - 66	46	25 - 77
Cu	23	22 - 42	48	34 - 76
Cd	2	1 - 6	5	2 - 8
Cr	9	8 - 14	21	10 - 27
Ni	2	1 - 4	4	2 - 8
Pb	4	2 - 7	9	8 - 28
Se	0.4	0.3 - 1.2	1.2	0.8 - 4.1

have long been recognized as sensitive indicators of environmental conditions. They are also good accumulators of many elements, Battal et al. 2004, Turhan et al. 2005, Ekmekyapar et al. 2006, Yazıcı and Aslan 2006, Bingöl et al. 2009), particularly heavy metals and radionuclides (Nayaka et al., 2003; Aslan et al. 2004, 2006, 2010).

Our objectives were to evaluate the effectiveness of eight lichen species as bioindicators of soil pollution from traffic activities. Specifically, we studied metal accumulation by four lichen species as impacted by (1) air emissions distance from roadside (0 and 100 m), (2) to predict heavy metals source from motor vehicles or natural parent material using enrichment factor (3) to test lichen biomonitoring a reliable tool to estimate traffic activities.

MATERIALS AND METHODS

Study area

Eight lichen species were collected from Erzurum province in July 2009 and they were identified in the laboratory of lichenology at the Department of Biology by Dr. Aslan (Aslan et al., 2002). Sample specimens have been stored in the herbarium of Kazım Karabekir Faculty of Education, Ataturk University, Erzurum (Turkey). These species are *Lecanora muralis* (Schreb.) Rabenh., *Xanthoria elegans* (Link.) Th. Fr., *Ramalina polymorpha* (Lilj.) Ach., *Rhizoploca crysoleuca* (Sm.) Zopf., *Peltigera rufescens* (Weiss) Humb., *Xanthoria candelaria* (L.) Th. Fr., *Cetraria islandica* (L.) Ach., and *Cetraria aculeata* (Schreb.) Fr. These species were collected from rock and soil. The study area is located (N 40° 14' 56", E 41° 31' 18") 1880 m altitude of the eastern part of Turkey. Eight sampling sites, which are situated along D-950 motorway in the section from the Erzurum to Tortum, were selected for this study. The motorway, carrying more than 20,000 motor vehicles per day, is the main road connecting Erzurum to Ardahan eastern part of Turkey. Soil and lichens samples were sampled from roadside located at 1100- 1880 m altitudes along the main road. The sampling point of the 1100 - 1880 altitude location started at 0 - 100 m distance from the edge of the motorway. Ten surface (0 - 10 cm) soil and 10 lichens samples per one altitude were collected within a 2000 m² area. Soil and lichens samples were packed into polyethylene bags and care was taken to avoid contamination from other sources such as industrial waste, dumping garbage,

wastewater effluents, or composts that might mask the real situation.

Soil and lichen analysis

Soil and lichen samples were air-dried, crushed, and passed through a 2-mm sieve prior to chemical analysis. Essential (Fe, Mn, Zn, Cu) and non-essential (Pb, Ni, Se, Cr, and Cd) metals were determined after wet digestion of dried and ground sub-samples using a HNO₃-HCl acid mixture 10 ml (1:3 v/v) for soil and HNO₃-H₂O₂ acid mixture (2:3 v/v) with three step (first step; 150°C, 70%RF, 10 min; second step; 180°C, 90%RF, 25 min and third step; 100°C, 40%RF, 5 min) in microwave (Bergof Speedwave Microwave Digestion Equipment MWS-2). Mertens, 2005a Fe, Mn, Zn, Cu, Pb, Ni, Se, Cr, and Cd were determined using an inductively Couple Plasma spectrophotometer (Perkin-Elmer, Optima 2100 DV, ICP/OES, Shelton, CT 06484-4794, USA) (Mertens, 2005b).

Statistical analysis

Data gathered from sampling area were subjected to analysis of variance (ANOVA) and mean separation was done using Duncan test at $P < 0.05$ of SPSS 13.0 (2004) statistical program, with distance (0 and 100 m) as fixed effect and replication as random effects.

RESULTS AND DISCUSSION

Essential (Fe, Mn, Zn, and Cu), non-essential (Pb, Ni, Se, Cr, and Cd) metal concentration of soil samples varied with distance (0 to 100 or over 100 m) from the road side. It was observed that motor traffic activity of roadside increased all of the metal content especially non-essential metal. There were statistical significant between the distances in respect of total element concentration (Table 1). Total Fe, Mn, Zn, Cu, Pb, Ni, Se, Cr, and Cd contents of the near to road side (1-100 m) were considerably higher than in samples taken far away from the road side (> 100 m) (Table 1). They decreased rapidly with the distance from those at the back ground level within 80 or 90 m transects. These metals originating from motor vehicles activities are distributed in

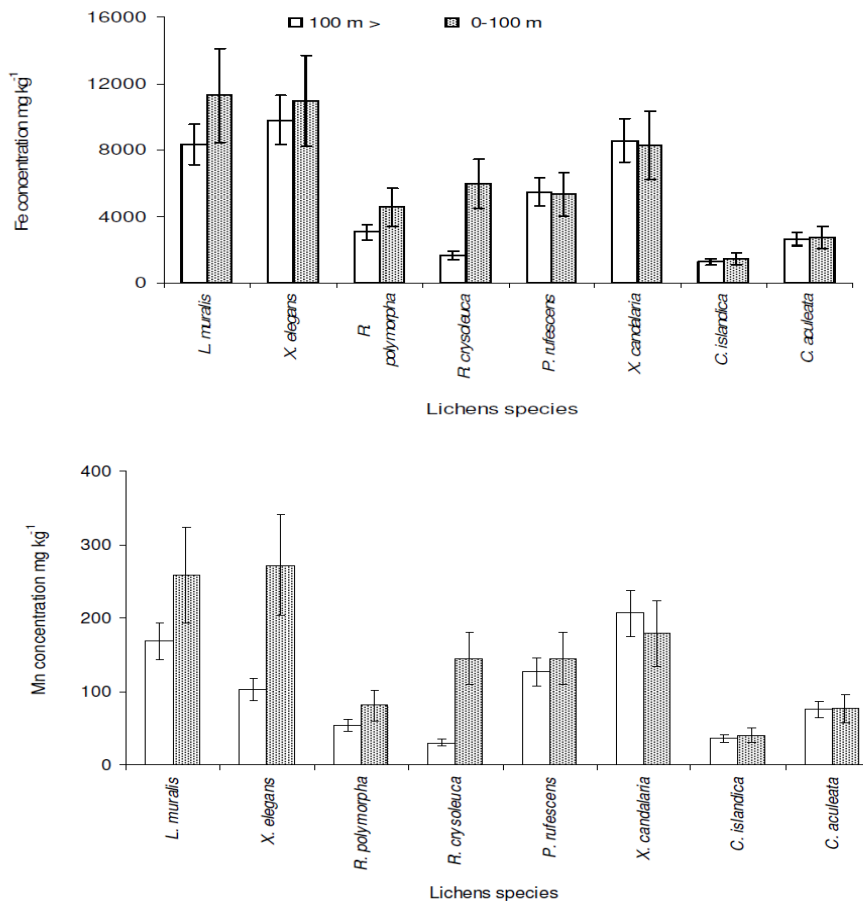


Figure 1. Impact on motor vehicles on distribution of concentration Fe, and Mn of soil and eight lichen species different distance from roadside.

soil by the atmosphere within a distance. Iron, Mn, Cu, B, Zn, Al, Cd, Cr, Ni, Se and Pb concentration of lichen species grown on unpolluted area (>100 m) were analyzed in this survey and they range from 1277-9806, 29.8-206.4, 0.1-8.4, 13.6-39.8, 2.6-4.3, 3.4-11.4, 1.4-8.2, 0.5-0.8 and 2.9-4.8 mg kg⁻¹, respectively but, roadside area (1-100 m) has got 1431-11293, 39.9-272, 0.3-37.5, 15.8-56.3, 2.9-6.9, 3.9-15.9, 2.4-22.4, 0.6-0.9 and 3.8-9.1 mg kg⁻¹, all of the element contents of lichens which is closest to the road had higher element content than lichens species which is 100 m far away from the road. This indicates that the available concentration of these elements in the study area may be lower than the fertile levels and the accumulation of these elements around the roadside soil, whether it is due to the air pollution from the traffic emission or deposits from the higher land erosion are still at reasonable levels.

The distribution pattern of total concentration of element can be used to judge whether the enrichment of an element is due to traffic pollution or from farming practices and natural erosion. As an index, the enrichment factor (EF) ($EF_{\text{soil}} = (M/Fe)_{\text{soil}} / ((M/Fe)_{\text{control}}$) is

also used to distinguish whether an element in soils are derived from natural or anthropogenic sources. According to Oliva and Espinosa (2007), enrichment factor values >2 were considered as a critical level of enrichment contributed mainly by anthropogenic inputs.

Essential metal content (Fe, Mn, Cu and Zn)

Iron is a common and rich element in soils and is an essential nutrient for all organisms. No literature has suggested a toxic level for this element. Leaded petrol and diesel oil contain high level of Fe even the unleaded petrol emission contains Fe in a lesser extent. Some reports have shown that traffic activities enrich the roadside soil Fe content (Monaci et al., 2000). However, Oliva and Espinosa (2007) concluded that the enrichment of Fe in roadside soil was attributed to the natural sources. Although Fe has been cited as a component of petrols and oils used for cars, this may be due to the fact that it is rich in soil and can be easily transformed (ranged from 1.1 to 1.4) (Figure 1). The total concentration

of Fe of soils in this area is already higher than the legal allowed level but the EF factor that were used by Oliva and Espinosa (2007) to distinguish pollution from the natural source was lower than 2. This is because its value is lower than the EF factor of Cr and Cd. We can conclude that the pollution of Fe in this area is due to the farming activities or natural existence. The highest Fe uptake was detected from *L. muralis* species.

Manganese is a common and rich element in soils and is an essential nutrient for organisms. Some reports showed that traffic activities enriched the roadside soil Mn content (Monaci et al., 2000), but Oliva and Espinosa (2007) concluded that that enrichment was attributed to natural sources. In general there is no toxic problem for upland crop, but ERD (1999) set the phytotoxic level for Mn at 220 mg kg⁻¹. The toxic trigger concentration was set at 70, 38 and 300 mg kg⁻¹ by ICRCL (1987), ERD (1999) and Efrogmson et al. (1997), while the Netherland government sets their target level at 35 mg kg⁻¹ (Zero, 2007), and Efrogmson et al. (1997) set it at 500 mg kg⁻¹. Accordingly, the concentration of total Mn of all soil samples (ranged from 280-480 mg kg⁻¹) in this study area were in toxic level (Figure 1). There was decrease of concentration of soil total Mn with the increase of distance from roadside. The highest Mn uptake was determined from *X. elegans* species. Although Mn like Fe has been cited as a component of petrols and oils used for cars, this may be because it is also rich in soil and can be easily transformed into steady forms of the EF factor of Mn in this area is also similar to Fe (ranged from 1.0 to 1.4) (Figure 1).

Copper is a trace element in most soils. It is an essential element for plants, animals, and people, but it also has a toxic element, which has been a major concern, to all organisms. The toxic trigger concentration was set at 130, 70 and 100 mg kg⁻¹ by ICRCL (1987), ERD (1999) and Efrogmson et al. (1997), while the Netherland government sets their target level at 36 mg kg⁻¹ (Zero, 2007). Accordingly, the concentraion of total Cu of all soil samples (ranged from 35-55 mg kg⁻¹) in this study area were in not toxic level.

Lot of literatures showed strong evidences that traffic activities is one of Cu pollution source on roadside soil (Monaci et al., 2000). However, whether the drift of the particulate can reach so high an altitude (201-400 m altitude) is not proved. This is a good support for the Cu pollution from the traffic activities but we still can not ignore pollution from the fertizer and manure (de Vries et al., 2002). The EF value of Cu ranged from 1.5 to 2.0, and increased as it approached the roadside (Figure 2). The highest Cu uptake was detected from *L.muralis* species. This can give a strong support to conclude that accumulation of Cu existed in this area and the accumulation rate is similar to Cd and Cr. They are main pollutant from traffic activities.

Zinc is a trace element in most soil especially in acid soils. It is an essential nutrient for all organisms. Zinc is a

common component in leaded petrol, diesel oil, and even in unleaded petrol and in tyre wear and brakes. Inevitably, Zn is a pollutant of traffic activities on roadside soils (Monaci et al., 2000; Oliva and Espinosa, 2007). The toxic trigger and action taken concentrations were set at 300 and 1665 mg kg⁻¹ by ICRCL (1987), while Efrogmson et al. (1997) set at 50 mg kg⁻¹, and the Netherland government sets their target level at 140 mg kg⁻¹ (Zero, 2007). The concentration of soil total Zn in the study area ranged from 25 to 70 mg kg⁻¹. Thus the soil data showed that the study area did not have Zn pollution. The pollution of Zn in arable lands was mainly from the fertilizers, especially from manure. The contribution of Zn from the atmospheric deposition is minor (de Vries et al., 2002). This illustrated that the source of Zn pollution in this area soil were mainly from farming activities and traffic activity affected area was only the land close to the main road (Figure 2). The EF values of Zn ranged from 1.1 to 1.5 and increased when it got closer to the roadside. This can give a strong support to conclude that traffic activities can partly contribute to Zn pollution in this area and actually, the main contibutors of Zn accumulation in this area are due to the farming activities. This illustrated that the pollution source of Zn in this soil area were mainly from the farming activities and the traffic activity did not affect the area (Figure 2). The EF values of Zn ranged from 0.9 to 1.1 and increased when it got closer to the roadside. The highest Zn uptake was determined from *X. elegans* species.

Non-essential metal content (Cd, Se, Cr, Ni, and Pb)

Cadmium is a trace element in most soil. It is not an essential nutrient of plant but a toxic element to plant, animal and human beings. Cadmium has been one of the most concerned heavy metal pollutant and some previous studies indicates that it is associated with motor traffic (Çiçek et al., 2008) and may be released by tyre wear. There is no strong evidence to prove that Cd pollution by the roadside soil was mainly from the traffic activities (Monaci et al., 2000; Oliva et al., 2007).

The total Cd concentraion of soil was decreased steadily with the increase of location distance and reached a constant level over 100 m far from the roadside. The accumulation of Cd in soil can be from traffic and agricultural activities. In the Netherlands, they found that the contribution of Cd on arable land from fertilizer was higher than the atmospheric deposition and that the phosphate and compound fertilizers were the first contributors (de Vries et al., 2002). The EF values of Cd ranged from 1.00 to 2.2 and increased when it got closer to the roadside (Figure 3). The EF value of Cd can be used as a good critical value to distinguish the pollution from traffic activities. The highest Cd uptake was detected from *X. candalaria* species. This can give a strong support to conclude that traffic activities are contributors

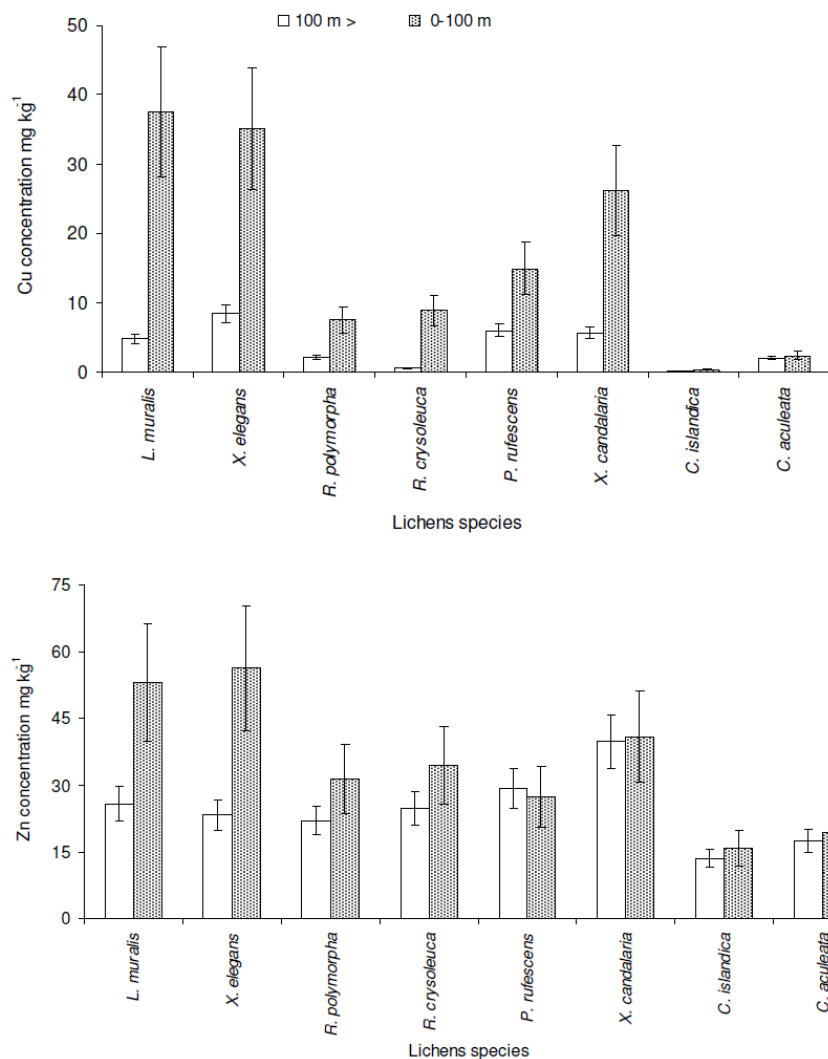


Figure 2. Impact on motor vehicles on distribution of concentration Cu, and Zn of soil and eight lichen species different distance from roadside.

to Cd pollution, but without a more sophisticated calculation it is impossible to weight how much is due to the traffic activities and farming activities. However this data gives a warning about the pollution of Cd in this area.

Selenium (Se) is a trace element in most soil and is an essential micronutrient for many organisms, including plants, animals and humans. As plants are the main source of dietary Se, plant Se metabolism is therefore important for Se nutrition of humans and other animals. However, the concentration of Se in plant foods varies between areas, and too much Se can lead to toxicity. Plant Se uptake and metabolism can be exploited for the purposes of developing high-Se crop cultivars and plant-mediated removal of excess Se from soil or water.

The metalloids selenium (Se) is ubiquitous in the environment, and its concentration in most soils ranges from 0.01 to 2.0 mg kg⁻¹, with a mean of 0.4 mg kg⁻¹;

however, higher concentrations (>10 mg kg⁻¹) can occur in seleniferous areas. Soil Se concentration and bioavailability vary with parent material and environmental conditions, and the distribution of Se in soils is usually heterogeneous and site-specific Wang and Gao (2001). However, Se bioavailability to plants can vary substantially for reasons that are still poorly understood. The EF values of Se ranged from 0.8 to 1.0 (Figure 3). This can give a strong support to conclude that the accumulation of CO existed in this area. The highest Se uptake was detected from *R. polymorpha* species.

Chromium is a trace element in most soil. It is not an essential nutrient of plant but is a trace essential element for animal and people. It is also a concern as it contains toxic element especially its Cr (VI) form. Monaci et al. (2000) investigated Cr concentration in soil beside the busy road and found no correlation with the traffic

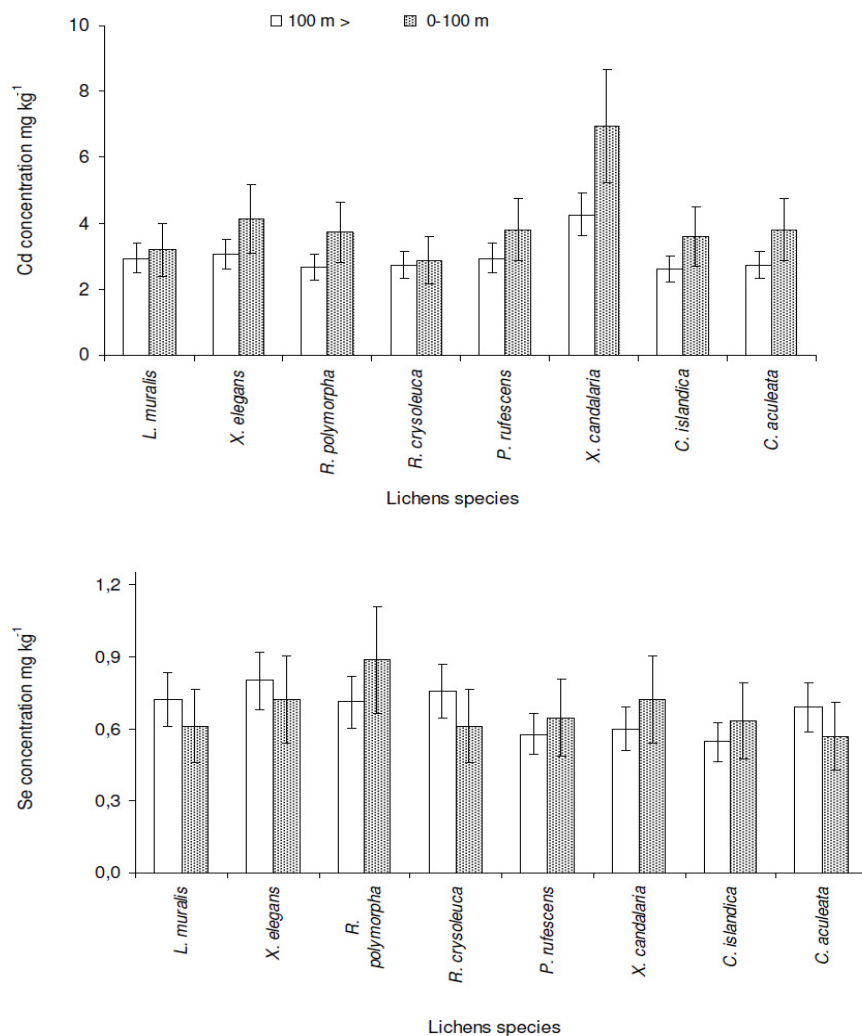


Figure 3. Impact on motor vehicles on distribution of concentration Cd and Se content of soil and some lichen species different distance from roadside.

activities. The concentration of total Cr in soils was decreased with the increase of destination far from the roadside and its concentration remained nearly constant over 100 m distance from roadside. The highest Cr uptake was determined from *X. elegans* species. The EF values of Cr ranged from 1.01 to 2.3 (Figure 4) and was increased when approaching the roadside. This can give a strong support to conclude that the accumulation of Cr existed in this area and the accumulation rate is similar to Cd, both of them are main pollutant from traffic activities. The EF value of Cd and Cr can be a good critical value to distinguish pollution from the traffic activities.

Nickel is a trace element in soils. It is an essential element for animals and some plants. Some reports found it was enriched in roadside soils but there was no direct evidence to conclude that enrichment came from

the traffic activities (Monaci et al., 2000; Oliva and Espinosa, 2007), although it was found in fossil fuel emissions. The toxic trigger concentration was set at 70, 38 and 300 mg kg⁻¹ by ICRCL (1987), ERD (1999) and Efrogmson et al. (1997), while the Netherland government sets their target level at 35 mg kg⁻¹ (Zero, 2007). The concentration of soil total Ni of all samples in the study area ranged from 2 to 3 mg kg⁻¹ (Figure 4). The concentration of Ni in lichen was very higher; it ranged from 1.1 to 22.2 mg kg⁻¹. There was decrease of concentration of soil and lichen total Ni with the increase of distance from roadside. The Ni concentration reached a constant level of over 100 m distance from roadside. This suggested that the soil near the main road was really polluted by traffic activities. The EF values of Ni ranged from 1.3 to 2.3 and increased with closing to the

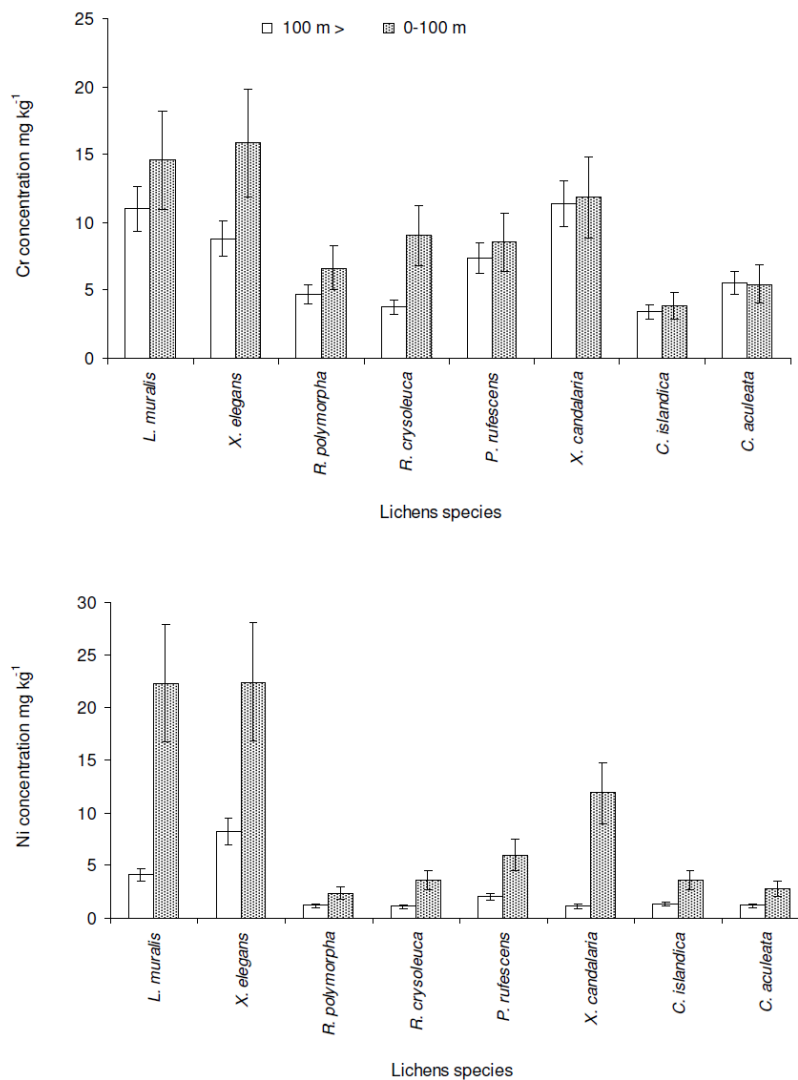


Figure 4. Impact on motor vehicles on distribution of concentration Cr, and Ni content of soil and some lichen species different distance from roadside.

roadside (Figure 4). The highest Ni uptake was detected from *X. muralis* species. This can give a strong support to conclude that traffic activities contributed to Ni pollution, but the status is not serious. When we used the EF values from Cd and Cr, we saw that soils within 100 m distance locations are strongly affected by traffic activities.

Lead is a trace element in soil and there has been concern about its toxicity to organisms. It has been used in leaded petrol, diesel oil, even in unleaded petrol ($<0.015 \text{ g L}^{-1}$) and there has been concerns that it is the main pollutant from traffic activities (Monaci et al., 2000, Oliva and Espinosa, 2007). The toxic trigger and action taken concentration was set at 500 and 813 mg kg^{-1} by ICRC (1987), while Efraymson et al. (1997) and ERD (1999) set at 50 and 120 mg kg^{-1} , respectively, and the

Netherlands government sets their target level at 85 mg kg^{-1} (Zero 2007). The concentration of total Pb in the study area was ranged from 4 to 12 mg kg^{-1} . Thus the soil data showed that the Pb pollution situation is not quite serious. The pollution of Pb from the fertilizers was minor when compared to the atmospheric deposition (de Vries et al., 2002). There was decrease of concentration of soil and lichen total Pb with the increase of distance from roadside. The Pb concentration reached to a constant level of over 100 m distance from roadside. The highest Pb uptake was detected from *X. candelaria* species. Hopefully the concentration of Pb in lichens was quite low; it ranged from 1.5 to 11.5 mg kg^{-1} . The EF factor of Pb ranged from 1.10 to 2.5 (Figure 5) and increased when getting closer to the roadside. This can give a strong

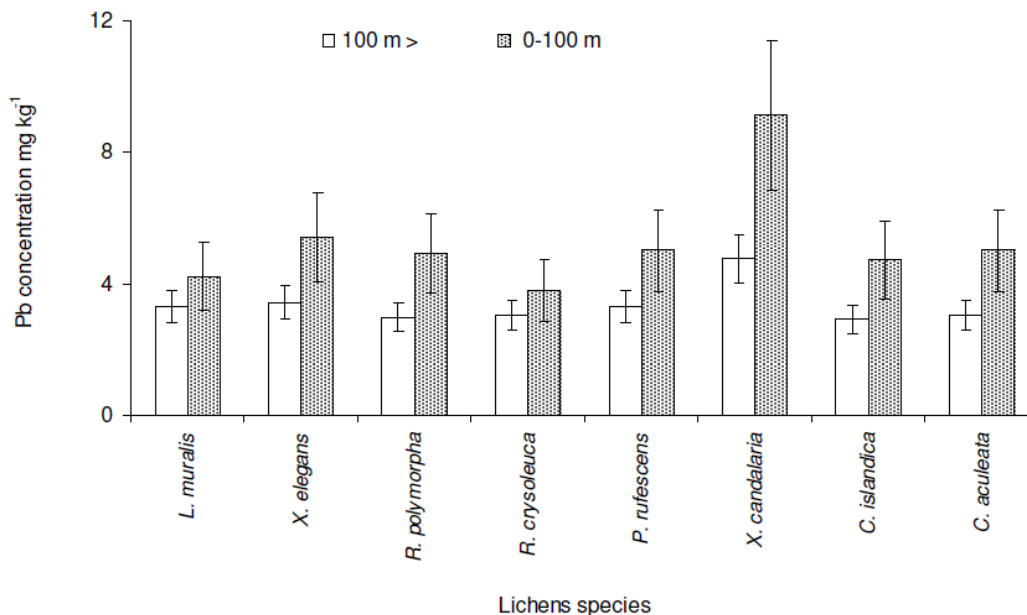


Figure 5. Impact on motor vehicles on distribution of concentration Cd, Se, Cr, Ni, and Pb content of soil and some lichen species different distance from roadside.

support to conclude that traffic activities are the main contributors to Pb pollution, and the drift of its emission can reach a distance of 100 m.

The results of this study showed that the contamination of roadside soils with heavy metals from the traffic activities is not a common problem along D-950 motorway, except Ni, Cd, Cr, Cu and Pb. The accumulation of all determined elements is inevitable because the erosion situation in this area is a common problem. The high accumulation of Fe and Zn are mainly from farming activities. The EF factor can use the value that proved they are not mainly from the traffic elements. Its critical value is about 1.5. As a conclusion, it can be said that appropriate safe distance should be selected in farming area for Ni, Cd, Cr, Cu and Pb over 100 m distance from roadside.

These findings suggest that lichen species *X. candelaria*, *L. Muralis*, and *X. elegans* present in the region can be used to monitor pollution of traffic origin and *X. candelaria* is, particularly, a very good indicator pollution of traffic origin. This is because lichens grow very slowly and are rarely encountered in polluted areas and lichen transplantation seems to be coming forward for air pollution monitoring. Transplantation of *X. candelaria* could be an easy and cost-effective means of air pollution monitoring and could provide valuable data for preventive measures. In this work, our goal was to contribute to lichen studies, which are of great importance for bio-monitoring, and this article reveals traffic-originated metal pollution using structural features of lichens. Further studies should be conducted for different soil profile depth from the roadside to determine

hyperaccumulator capacity of lichen species across the region.

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