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Lichens as a Monitor for Atmospheric Manganese Pollution

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Abstract: This study presents results obtained after lichens, *parmelia sulcata*, was used to investigate manganese concentrations near roadside environments. It was observed that the average manganese concentration in the study area, 540.032±19.896 mg/kg, exceeded the background concentration by a factor of about 1.03. The manganese concentration on the eastern and western sides of the road exceeded the background by factors of 1.05 and 1.01, respectively. P4 ranked first in Mn levels in the zone with a concentration of 1561.763±10.754 mg/kg, exceeding the background concentration by a factor of 2.97. Other observations showed that an inverse relationship exists between the suspected source of Mn emission and the proximity to the road. Traffic studies conducted in the study area also revealed that Mn emission could be directly proportional to the traffic volume.

Key words: Emission, environmental pollution studies, lichen transplants, manganese, traffic volume

INTRODUCTION

Manganese (Mn) is ubiquitous in the environment and comprises about 0.1% of the Earth's crust. Crustal rock is a major source of manganese found in the atmosphere. Ocean sprays, forest fires, vegetation and volcanic activity are other major natural sources of atmospheric manganese. Anthropogenic releases include emissions from alloy, steel and iron production and combustion of fossil fuels.

Manganese is very useful in many ways. It is commonly used in steel industries and in the production of dry cell batteries. The element is also essential for the proper functioning of humans, plants and other animals, as it is required for the functioning of many cellular enzymes like pyruvate carboxylase (IPCS, 2002). Compounds of manganese are used as oxidizing agents in qualitative analysis and in medicine. Still, other manganese compounds are used in fertilizers, varnish and fungicides and as livestock feeding supplements (HSDB, 2001). An organic manganese compound, Methylcyclopentadienyl Manganese Tricarbonyl (MMT), is used as an octane-enhancing agent in unleaded petrol.

Like most trace elements, though Mn is useful, it is also known to cause harm to the environment at certain elevated concentrations. Symptoms of manganese toxicity to terrestrial plants vary widely with species. They include marginal chloroses, necrotic lesions and distorted development of the leaves. Of great concern are the harmful effects on humans. Studies have shown that fine particles containing manganese can be absorbed into the blood through the lungs and ferried directly into the central nervous system and the brain Abundant evidence collected in occupational settings indicates that chronic exposure to inhaled manganese compounds can lead to a progressive neurologic syndrome known as *manganism.* Symptoms of manganism include impaired coordination and motor skills, nervousness and hyperirritability and psychiatric disturbances including hallucinations (Dobson *et al*., 2004).

Methylcyclopentadienyl Manganese Tricarbonyl (MMT) forms manganese particles when burned as a gasoline additive. Combustion products of MMT are mainly a mixture of Mn phosphate and Mn sulphate. These particles can be emitted to the atmosphere or deposited on engine and vehicle components, causing concern in either case. Manganese can be a potent neurotoxin when inhaled (ATSDR, 2000). It is for these reasons that MMT, though approved in other countries, is not in intensive use in other countries. Even after several years of use of MMT in Canada and other countries, many uncertainties remain. Research raises major concerns with regard to public effects related to exposure to Mn (Loranger and Zayed, 1997).

With the phasing out of lead based antiknocks for gasoline by a legislative instrument amendment regulation, the manganese-based antiknock, Methylcyclopentadienyl Manganese Tricarbonyl (MMT) has been introduced on the Ghanaian market since 2004. After nearly 2 years of its usage, this study seeks to use

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lichens to investigate manganese concentrations near roadside environments as against background concentrations.

MATERIALS AND METHODS

Sampling area: The study area is the Madina-Tetteh Quarshie Road in the Greater Accra Region of Ghana. This road which spans a distance of about 4.6 km is located between latitudes N 05º37′52.4″and N 05º40′01.1″ and longitudes W 00º10′36.9″ and W 00°10′37.5″. This is the major road that connects people living in Adenta, Madina, Ashaley Botwe, Haatso, Agbogba, Ashongman all in the Ga District of the Greater Accra region. Vehicles traveling from parts of the Eastern and Volta Regions of the country to the capital city, Accra, also ply this road. Important features along the road are the University of Ghana, Legon, Presbyterian Boys' Secondary School (PRESEC), Ghana Standards Board and four fuel filling stations. The major economic activities in the area are peasant farming, sale of food and household items, sand and gravels. There are no industrial activities in the area.

Fourty-one sampling points were located in the study area. The portion of the Madina-Tetteh Quarshie road, which was of interest, covers the Atomic Junction to the Tetteh Quarshie Interchange. This spans a distance of about 4.6 km. A map of the study area with sampling points shown in Fig. 1.

The 41 points were located at intervals of 100 m. Twenty-one points were on the western side of the road and 20 on the eastern. The points were located at distances ranging from 2 m to 38 m off the road using a measuring tape and then a Geographic Positioning System (GPS). To investigate changes in manganese concentration with distance from the source of emission, two transplants were located at different distances in succession off the road behind sampling point P41. Another set of three transplants was located at sampling point P9 on the other side of the road.

Sampling and sample preparation: Lichens together with its substratum were collected from the barks and trunks of old cocoa and other trees at about 2 m above the soil from a forest in Tafo in the eastern region in the November 2004. This area was considered clean from pollution point of view. It therefore served as the control area. Using disinfected knives, the lichens were collected and bagged in polythene bags. Disposable plastic gloves were used in handling the lichens to avoid contamination (Sansoni and Iyengar, 1978; Sloof, 1993). The lichens, identified to be *Parmelia* sp., were put in lichen bags sewn from nylon mesh and suspended on support systems made of bamboo, located at the sampling points. The height of suspension was about 1.5 m above the ground. A total number of 51 transplants were used. Regular inspection was carried out at the sampling points. The lichens were suspended in November 2004 and removed in February 2005. At the time of removal, 3 samples were lost. The transplants were removed into polythene bags using disposable plastic gloves to avoid contamination (Sansoni and Iyengar, 1978; Sloof, 1993).

In the laboratory, the lichen samples were removed from the nylon and the polythene bags. They were then washed in de-ionized water to remove dust and sand. In this washing procedure, the lichen samples were immersed in the water for about 30 sec and removed (Sansoni and Iyengar, 1978; IAEA, 1980; Markert, 1993). These were then placed on clean transparent polythene sheets and air-dried for 48 h. The dried lichens were then scrapped gently from the tree barks using lancets. The lichens of the control sample were also scrapped. The fine powder of lichen samples was obtained by manual grinding in an agate mortar. The control lichens samples, i.e., lichens which were not transplanted or suspended, were also prepared in a similar fashion. About 150 mg of the lichen powder was weighed in small polythene sheets and wrapped. Representative samples of each lichen transplant were prepared in duplicates. The wrapped lichen samples were heat-sealed in plastic vials for irradiation. With the Comparator method, a standard of Mn was also prepared and irradiated. For analytical quality assurance, 150 mg of Standard Reference Material (SRM), Oyster tissue was also prepared and irradiated under the same conditions.

Irradiation and counting of samples: The irradiation of the samples was performed in the Ghana Research Reactor-1 (GHARR-1), which is a miniature source (MNSR). GHARR-1 adopts the pool-tank structure, employs highly enriched uranium (90.2% ^{235}U) as fuel, light water as moderator and coolant, and beryllium metal as reflector. The thermal power of GHARR-1 is 30 kW corresponding to a neutron flux of 1×10^{12} n/cm^{2}s. GHARR-1 has ten irradiation sites of which five are inner and five outer. Irradiation of the samples was carried out with the reactor operating between 3-15 kW with a neutron flux of 1-5$\times10^{11}$ n/cm^{2}s in one of the inner irradiation. The samples were irradiated for 60 sec and counted for 600 sec using the PC-based gamma-ray spectroscopy system consisting of an N-type High Purity Germanium (HPGe) detector (model GR 2518), High Voltage (HV) power supply, (model 3105), an amplifier (model 2020) -all manufactured by Canberra Industries Inc., an 8k Multi-Channel Analyzer (MCA) emulation software and a micro-computer for spectrum collection and evaluation. The detector operates on a bias voltage of ($-V_e$) –3000 V and has a resolution of 1.8 keV for Co-60 gamma ray energy of 1332 keV. The samples and the comparator were counted at a distance of 7.2 cm from the top of the detector surface to quantify the element.

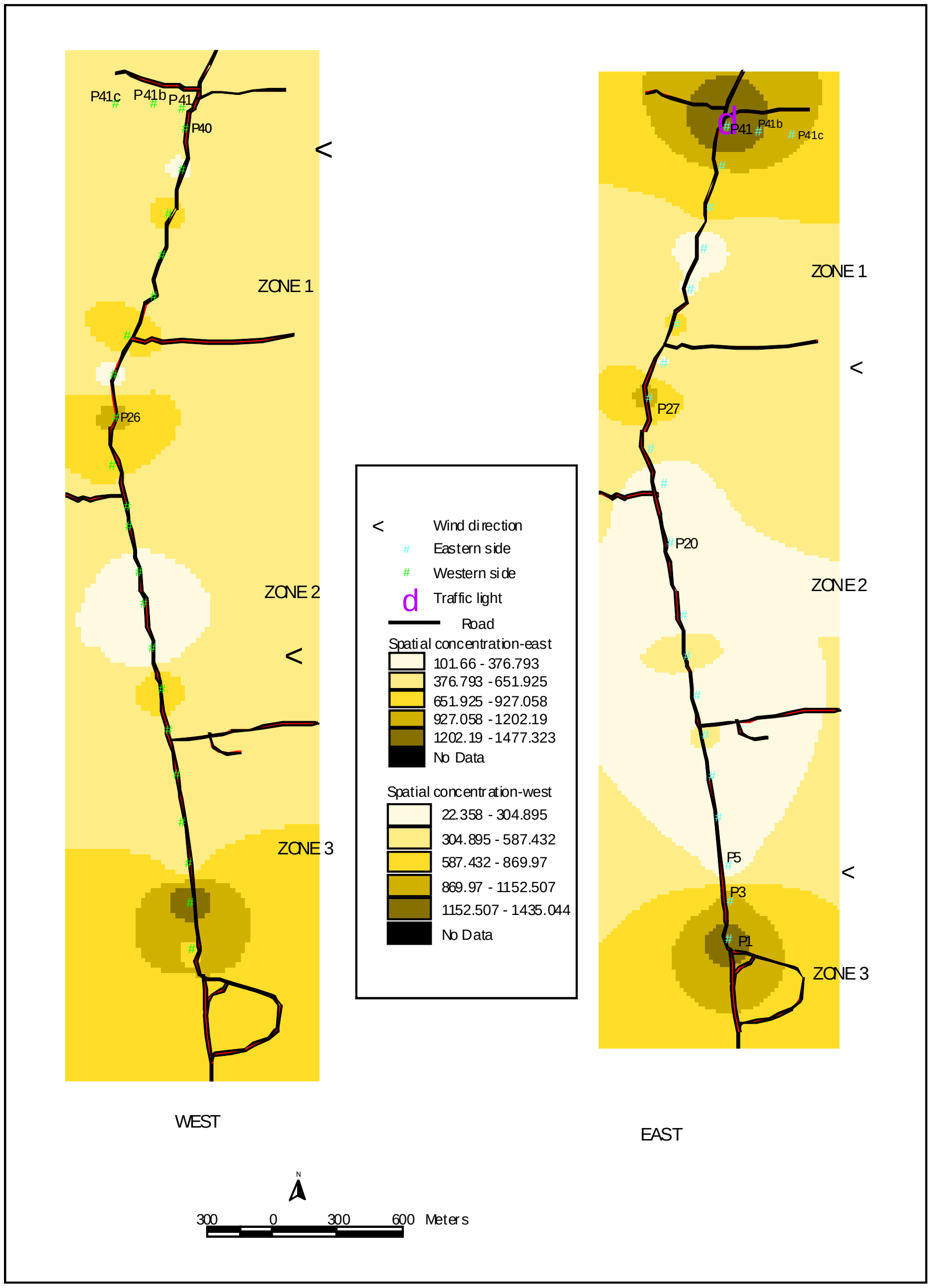

Fig .1: Manganese F concentration along the Madina-Tetteh Quarshie Road

Mn concentration determination: The comparator method was used to calculate the concentration of manganese in the lichen samples. In this method, a standard containing a known amount of the element to be determined is irradiated with the sample. It is assumed that the neutron flux, cross section, irradiation times and all other variables associated with counting are constant for the standard and sample at a particular sample-to-detector geometry. The manganese concentration was then calculated using the neutron activation equation below:

$$c_{sam} = \{ [(P_A / t_c)\ CD]_{sam} \cdot [cW]_{std} \} / [(P_A / t_c) CD]_{std} \cdot W_{sam}]$$

where $(P_A / t_c)_{std}$ and $(P_A / t_c)_{sam}$ are the counting rates for standard and sample respectively, c_{std} and c_{sam} are the

Table 1: Manganese concentrations in lichen transplants along the Madina-Tetteh Quarshie road

Eastern side sampling points	Distance off road, m	Manganese conc., mg/kg	Western side sampling points	Distance off road, m	Manganese conc., mg/kg
Control	-	525.84±9.736	Control	-	525.84±9.736
1	8	1400.130±12.806	2	23	859.214±6.940
3	26	1212.670±8.999	4	3	1561.763±10.754
5	38	157.863±2.885	6	15	459.760±4.439
7	11	147.685±1.353	8	5	344.485±4.259
9	5	260.876±5.687	10	12	337.145±5.558
11	15	419.034±4.157	12	7	-
13	8	101.187±3.377	14	2	783.91±7.434
15	11	569.588±28.4764	16	7	17.470±1.636
17	4	230.638±4.846	18	5	165.103±0.703
20	11	-	19	12	190.125±1.940
23	33	158.407±2.593	21	3	445.970±4.021
25	10	514.410±4.584	22	5	458.207±4.295
27	2	1042.856±7.890	24	15	679.405±5.149
29	6	363.552±5.120	26	4	1027.024±8.650
31	3	701.415±8.999	28	30	161.635±2.836
33	5	354.245±4.168	30	30	787.573±5.823
35	12	153.956±2.543	32	4	498.792±5.701
37	8	851.604±6.574	34	10	455.245±3.531
39	18	-	36	15	659.466±5.194
41	5	1477.354±10.257	38	4	247.197±6.281
			40	28	565.616±4.879
Mean		550.970±15.248			529.095±24.544

concentrations of the element of interest in standard and sample respectively, W_{sam} and W_{std}, the weight of the sample and standard respectively, C_{std} and C_{sam} are the counting factors for standard and sample, D_{std} and D_{sam} are decay factors for standard and sample respectively.

RESULTS AND DISCUSSION

The results obtained for the NAA of the standard reference material in this work was 20.135±1.70 mg/kg while the reported value was 18.50±0.20 mg/kg. The precision of the results were calculated as percentage relative standard deviation (%RSD) of six replicate measurements and were found to be within 10%. The results of the manganese analysis of the lichens transplants are shown in Table 1. The manganese concentrations shown, i.e., due to motor vehicles, was obtained by subtracting the background manganese concentration from the total manganese concentration accumulated by the lichen transplants over the 3-month study period.

Mean Manganese concentration: It was observed that the average manganese concentration in the study area, 540.032±19.896 mg/kg, exceeded the background concentration by a factor of about 1.03 while the mean eastern and western sides exceeded the background by factors of 1.05 and 1.01, respectively. Whereas there exists other possible sources of Mn in roadside environments, it is clear that indeed motor vehicles, which use the Mn-based antiknock, contribute significantly to atmospheric Mn along roadsides. Mn was also detected in extremely high amounts (13680±1153 mg/g) in plants at a distance of 2 m away from a motorway in Utah, USA (Lytle *et al*., 1994). High Mn values detected in the feral pigeon (*Columba livia*) (Loranger *et al*., 1994; Sierra *et al*., 1998) and in different plants used as monitors in Canada (Brault *et al*., 1994; Forget *et al*., 1994; Normandin *et al*., 1999) referred to the same origin.

Variation of Manganese concentration within the study area: In order to facilitate a discussion of the variations, the study area was divided into 3 zones. Zone 1 spans from Atomic Junction to IPS Junction (ATJ-IPSJ), zone 2 from IPS Junction to Okponglo Junction (IPSJ-OKPJ) and zone 3 Okponglo Junction to Tetteh Quarshie Roundabout (OKPJ-TTQR).

Zone 1: This zone covers the area from "Atomic Junction" and "IPS Junction" with sampling points P33-P41. P41 was located 3 m off the road from a traffic light at the intersection of "Haatso-Atomic and Madina-Tetteh-Quarshie highways". This zone has 4 bus stops and experiences considerable heavy vehicular traffic, which aggravates as one approach the traffic light at the intersection. The major economic activities in the area are selling of food and household items by vendors, sand and gravels trade along the road especially on the western side and peasant farming.

Figure 1 shows the Mn distribution in the study area. It was observed that high manganese concentrations were accumulated at sampling points P1, P3, P4 and P41 all located very close to a traffic light and a point of convergence of 2 roads. P4 ranked first in Mn levels in the zone with a concentration of 1561.763±10.754 mg/kg, exceeding the background concentration by a factor of 2.97. These extremely high concentrations can be

Table 2: Traffic volume on the Madina-Tetteh quarshie road

Morning rush hour 7 - 8 AM	Vehicles driving on TTQR – OKPJ road (ZONE 3)		Vehicles driving on OKPJ – IPSJ Road (ZONE 2)		Vehicles driving on IPSJ - ATJ Road (ZONE 1)	
Day	Southbound	Northbound	Southbound	Northbound	Southbound	Northbound
Monday	2800	918	2100	900	2730	890
Tuesday	2757	890	1921	890	2610	900
Wednesday	2840	900	2060	902	2482	886
Thursday	2700	850	1953	830	2712	918
Friday	2860	950	2006	861	2525	903
Evening rush hour 6 -7PM						
Monday	950	3000	890	1510	880	3000
Tuesday	892	2876	886	1332	862	3010
Wednesday	835	2853	856	1568	736	2980
Thursday	920	2990	790	1499	799	2871
Friday	899	2865	782	1520	865	2918

explained by the higher abrasion of car engines running idle near traffic lights, which releases particulates, in this case Mn, into roadside environments. This explanation is supported by the traffic volume counts, which were measured in the study area (Table 2).

Comparable data was obtained by Monaci *et al*. (1997) for *Flavoparmelia caperata* in Siena (Central Italy). Traffic was found to be the main source of atmospheric pollution. Also the amounts of Pb, Zn and Cd in transplanted thalli of *flavoparmelia caperata* were found to correlate positively with the accumulation of traffic on the western side of A1 motorway in France (Cuny *et al*., 2001).

Zone 2: This zone covers the area between the "IPS junction and the Okponglo junction". Sampling points P13-P32 fall within this zone. The zone is well vegetated on both sides of the road especially on the western side. It has few farmlands, 2 lorry stations, 7 bus stops, 3 fuel stations, electricity substation, a police station, a laundry and a bank. The University of Ghana is also located within this zone. This portion of the study area in this zone has 3 other roads joining it at certain points-one from the University, one from the University hospital and another from Okponglo.

In the entire zone, sampling points P27 and P26 recorded the third and fourth highest manganese concentrations of 1042.856±7.890 and 1027.02±8.65 mg/kg respectively. The high Mn concentrations were unexpected at these two sampling points. Higher Mn concentrations were expected at P21, P22 and P24 which were located near two bus stops and an intersection, rather than at P26 and P27. The lower levels of manganese concentrations at P21, P22 and P24 and generally in the entire zone, as shown in Fig. 1 can be attributed to its low traffic volume counts as shown in Table 2. Even during the rush hours, it is the western side of the road which experiences much of the traffic as more people move towards the city centre than return from it. This explains why the Mn concentrations are lower on the eastern side in this zone as shown in Fig. 1. During other periods of the day, however, the traffic flow is rapid, relative to what pertains in zones 1 and 3.

Zone 3: This zone begins from the "Okponglo junction" to the intersection of the "East Legon" Bypass and the" Madina-Tetteh Quarshie Road". Sampling points P1-P12 are located in this zone. Zones 1 and 3 are similar in terms of road network and traffic flow and the only major difference being the absence of a traffic light. There are also two minor parallel roads lying on the eastern side of the main "Madina- Tetteh Quarshie" road. These two roads, which eventually join the main road, are separated by a distance of 50 m from each other. The two minor roads experience heavy vehicular traffic congestion comparable to that on the main road during the morning rush hour as vehicles try to avoid the heavy traffic on the main road. This scenario results in even more vehicular traffic at the intersection as vehicles struggle to join the main road. The main road in this zone is also joined at a point by two roads from the University community. There is a filling station, two car-fitting workshops and few houses. The zone also houses the offices of some organizations including the Ghana Standards Board. The major economic activity is carpentry and car fitting. Though this zone also has good vegetation, much of it is replaced by buildings as one approaches the interchange.

Expectedly, P4 and P1 recorded values of 1561.763±10.754 and 1400.130±12.806 mg/kg respectively for Mn. These values represent the second and third highest Mn concentrations in the entire study area. These high values are as a result of the heavy vehicular traffic congestion. The other sampling points, i.e., P5-P11, recorded concentrations close to the mean manganese concentrations.

Variation of Manganese concentration with proximity to road: Variation of Manganese concentration with

Table 3: Variation of Manganese concentration with proximity to road

Sampling point	Distance off road (m)	Manganese concentration (mg/kg)
41:1	5	1477.741±10.257
41:2	15	1010.871±35.043
41:3	30	650.402±20.970
9:1	5	260.876±5.687
9:2	15	201.852±4.136
9:3	30	136.462±3.627

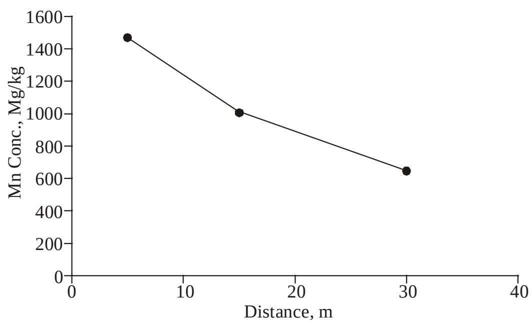

Fig.2: A graph of Mn Conc., mg/kg against distance, m at sampling pt 41

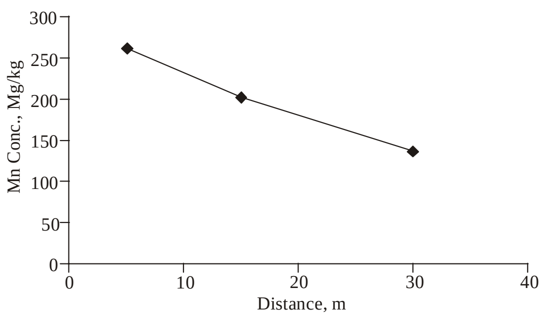

Fig. 3: A graph of Mn Conc., mg/kg against distance, m at sampling pt P9

proximity to road is shown in Table 3. Results obtained for sampling points P41 and P9, as shown in Table 2 and Fig. 2 and 3, indicate an abrupt decrease of manganese concentration occurring at a distance of 10 m. Lichens transplants showed a decrease in manganese concentration with increasing distance from suspected source of emission. The trend was also observed by Kapu *et al*. (1991) who used the bioaccumulative properties of *Parmelia* sp. to assess the aerial fallout of heavy metals from traffic in Zaria, northern Nigeria. Metal concentrations in epiphytic lichens decreased significantly with distance from Zaria/Samaru-Sokoto Highway but showed no significant difference along the residential road in the Samara Campus, Ahmadu Bello University, Zaria.

CONCLUSION

The following conclusions can be drawn from the above research study:

- An inverse relationship exists between the distance from the source of pollution and the manganese concentration accumulated by lichens
- Mn emission could be directly proportional to the traffic volume
- Populations with potential high exposures are those living near traffic lights
- Persons living close to high-density traffic areas, automotive workers, roadside vendors and drivers may be exposed to higher manganese arising from MMT combustion

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REFERENCES

ATSDR, 2000. Toxicological profile for manganese Atlantic, G A, US Department of Health and Human services, Public Health Service, Agency for Toxic Substances and Disease Registry

Brault, N., S. Loranger, F. Courchersne, G. Kennedy and J. Zayed, 1994. Bioaccumulation of manganese by plants: Influence of MMTas gasoline additive. Sci. Total Environ., 232: 67-77.

Cuny, D., C. Van Haluwyn and R. Pesch, 2001. Biomonitoring of trace elements in air and soin compartments along the major motorway in France. Water, Air Soil Pollut., 125: 273-289.

Dobson, A.N., M. Erikson and K.M. Aschner, 2004. Manganese neurotoxicity. Ann. NY Acad. Sci., 1012: 115-128

Forget, E., F. Courchersne, G. Kennedy and J. Zayed, 1994. Respose of blue spruce (*Picea pungens*) to manganese pollution from MMT. Water, Air Soil Pollut., 73: 319-324.

HSDB, 2001. Manganese Compounds, Bethesda, MD, National Library of Medicine, Hazardous Substances Data Bank. Retrieved from: http://toxnet.nlm.nih.gov/ cgi-bin/sis/htmlgen.

International Atomic Energy Agency (IAEA), 1980. Elemental Analysis of Biological materials, IAEA Technical Report Series No. 197, Vienna.

International Programme on Chemical Safety (IPCS), 2002. Manganese and its Compounds: Environmental Aspects. WHO, Geneva (Concise International Chemical Assessment Document 63).

Kapu, M.M., M.M. Ipaye, R.A.I. Ega, H.O. Akanya, M.L. Balarabe and D.J. Schaeffer, 1991. Lichens as bioindicators of aerial fallout of heavy metals in Zaria, Nigeria. Bull. Environ. Contam. Tox., 47(3): 413-416.

Loranger, S. and J. Zayed, 1997. Environmental contamination and human exposure to airborne total and respirable manganese in montreal. Air Waste Manage., 47: 983-989.

Loranger, S., G. Demers, G. Kennedy, E. Forget and J. Zayed, 1994. The pigeon (*Columba livia*) as a monitor for manganese contamination from motor vehicles. Arch. Environ. Contam. Toxicol., 27: 311-317.

Lytle, C.M., C.Z. McKinnon and B.N. Smith, 1994. Manganese accumulation in roadside soil and plants. Naturwissenschaften, 81: 509-510.

Markert, B., 1993. Plants as Biomonitors. Verlag Chemie, Weinheim and New York.

Monaci, F., R. Bargagli and D. Gasparo, 1997. Air pollution monitoring by lichens in a small medieval town of central Italy. Acta Bot. Neerl., 46: 403-412.

Normandin, L., G. Kennedy and J. Zayed, 1999. Potential of dandelion (*Taraxacum officinale*) as a bioindicator of manganese arising from the use of MMT in unleaded gasoline. Sci. Total Environ., 239: 165-171.

Sansoni, B. and V. Iyengar, 1978. Sampling and sample preparation methods for the analysis of trace elements in biological materials, Jul-Spez 13, Julich FRG.

Sierra, P., S. Chakrabarti, R. Tounkara, S. Loranger, G. Kennedy, E. Forget and J. Zayed, 1998. Bioaccumulation of manganese ad its toxicity in feral pigeons (*Columba livia*) exposed to manganese oxide dust (Mn_3O_4). Environ. Res., 79: 94-101.

Sloof, J.E., 1993. Environmental Lichenology: biomonitoring trace-element air pollution. Ph.D. Thesis, Delft, The Netherlands, pp: 191.