ASSESSMENT OF TOXIC METAL CONTAMINATION LEVEL AND ITS CHEMICAL SPECIATION IN AN URBAN ENVIRONMENT BY ROADSIDE TREE BARK MONITORING

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ABSTRACT

Roadside tree bark is an essential bio-monitor to assess the quality of the urban air environment. Due to the toxic properties of trace metals, it becomes lethal for non-human and humans biota, particularly in urban areas. The principal objective of this research has been to resolve the contamination of roadside tree bark in Guwahati and to specify their potential origin sources. In total 20 tree barks as well as deposited road dust samples were collected from 20 different locations of five various land use kinds covering Industrial, City Roadside, Commercial, Sensitive and National Highway Side within the Guwahati city roads characterized through varying vehicular traffic intensity. The heavy metal contamination in the roadside tree bark samples followed the order as Fe>Zn>Mn>Pb>Co>Cu>Ni>Cd>Cr while the road dust follows Cd<Co<Pb<Cr<Cu<Ni<Zn<Mn<Fe. The chemical speciation study in tree bark samples showed that Fe along with Mn is combined to Fe-Mn oxide fraction, Pb along with Ni is mostly associated with the replaceable fraction and Cd, Zn, Cu are destined to organic matter as well as Co to the residual or lattice fraction. The contamination level was evaluated with extensively established several pollution indices. Most of the indices showed that the tree barks were significantly polluted with Pb, Zn, Cu, Ni, Cd, and which is linked with anthropogenic factors (motor Traffic). The potential ecological risk in different zone showed the order National Highway Roadside > City Roadside > Commercial > Industrial > Sensitive.

Keywords: Heavy Metals, Tree Bark, Chemical Speciation, Pollution Indices

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INTRODUCTION

Heavy metals can come from several various causes in urbanized regions. In an urban environment, vehicular emissions are a major source for heavy metal exposure.¹⁻³ Heavy metals that appeared in street dust like Ni, Cu, Cr, Zn, Cd, Mn, along Pb are important for environmental pollution. As per the types of vehicles in traffic, the type and quantity of heavy metals differ from street dust. Heavy metal may gather on top of the soil from atmospheric deposition through interception, impaction and sedimentation. Pollution due to heavy metals from atmospheric deposition in urban regions is mainly indicated by road dust and topsoil and its persistence in the soil is a long practice. Lead as well as other dust metals are the main reason for the pollution near the roadside due to heavy traffic.^{4,5}

Following expression gives an easy mass balance of heavy metals in the soil:^{6,7}

$$M_{\text{total}} = [M_p + M_a + M_f + M_{\text{ag}} + M_{\text{ow}} + M_{\text{ip}}] - [M_{\text{cr}} + M_{\text{l}}]$$

Here, heavy metal is represented by “M”, “p” represents parent material, atmospheric deposition is represented “a”, where “f” belongs to fertilizer sources, agrochemical sources is showed by “ag”, organic waste sources is represented by “ow”, inorganic pollutants is showed by “ip”, “cr” represents crop removal, as well as leaching losses and volatilization, are represented by “l”. It's proposed the anthropogenic emission towards the environment for many heavy metals, is 3 orders of magnitude more compared to healthy fluxes.⁸ Anthropogenic resources produced more heavy metals and are usually more bioavailable as compared to lithogenic or pedogenic.^{9,10} Heavy metal can build up grow barks from atmospheric deposition through interception, sedimentation as well as impaction. Plants growing in areas with clean air but showing elevated heavy metals in the roots are probably being exposed in the sediments and soils in which they are growing.¹¹

Moreover, the uptaking of metal is dependent upon species of plants as well as affected by elements' interactions in soil solution. Metals are taken through plants from soil and are considered as the main path for measuring the risk of chemical impurities in soil.¹² In soil, the existence of toxic metals may rigorously inhibit the biodegradation of natural pollutants. Metal contaminated soil can lead to various hazards as well as risk to the ecosystem along with human through different ways such as direct consumption or contact with a decrease in land usability for cultivation, phytotoxicity, consuming polluted groundwater, "soil-plant – human or soil-plant – animal-human" food chain, polluted soil.¹³⁻¹⁵ The total concentration of heavy metal in the environment cannot give full information about the toxicity, bioavailability as well as capacity for remobilization risk for heavy metals. Nevertheless, only bioavailability prediction is known for heavy metals due to their chemical speciation. There are also some other factors such as bonding strength, both in complexed or free ionic form through natural material or integrated into the mineral portion of test. The focus or target in the research work is for checking the concentration levels of heavy metals in tree bark along with clarification of the chemical present in the environment, due to the good relation between speciation as well as toxicity. There are many extraction schemes presents to separate various chemical phases with which the metal is linked in various amounts.^{16,17}

EXPERIMENTAL

Site Description and Sampling

In this research work, Guwahati has been chosen to monitor the urban tree bark regarding trace metal composition ("91°33'E–91°52'E and 26°08'N–26°14'N"). Guwahati is the capital of Assam, India.

Assam is encompassed by the Brahmaputra River that is the biggest river in the whole world, in the north as well as the southern part it is covered by little and medium hills. This kind of hill shows up in nearly all aspects of the community, which has a complete part of 231 km² for the present population of about 3.2 million. The community may be the primary corridor for passage on the neighboring 7 states of India with the 2 freeways NH37 and NH31 passing through the community, are active with vehicular traffic morning and evening. Most of the roads are narrow in comparison to the volume of plying vehicles due to unplanned construction and rapid haphazard growth. Traffic jams have become very common even.

The roadside tree bark samples (Table-1) were collected along with the major ways in Guwahati. Five different kinds of zones were chosen for this study. These zones are located along (i) Industrial area with medium traffic (ii) City roadside located on the highly trafficked road (iii) Commercial and non-industrialized area with high traffic (iv) Sensitive zone having university with medium traffic (v) National Highway Roadside (NH37) with highly trafficked. In total 20 locations were chosen covering all the five zones (Fig.-1), and from every location, approximately (length=12 cm and breath=8 cm) a thin layer of roadside matured tree bark samples at 150 – 200 cm height above ground. Again, several deposited street dusts on the roots were also collected and mixing them thoroughly to make a composite sample from each location of the same tree.¹⁹ Samples have been transmitted in Polythene bags aseptically to the laboratory as well as wiped in a shade lumps have been damaged along with the fraction passing through ~94 µm sieve has been preserved for this research.¹⁸

Table-1: Various Street Dust and Tree Bark (with Local and Scientific Name) Samples collected from Different Zones of Guwahati

S. No.	Sampling Locations	Type	Local Name	Scientific Name
1	Noonmati (Near Petrol Depot)	Industrial	Mirzari	Casia siamea Lamk.
2	Noonmati-Chunsali Road		Banyan tree	Ficus bengalensis
3	Noonmati (Near Refinery)		Jack Fruit	Artocarpus
4	Bamunimaidan (Udyog Bhawan)		Bakul	Mimusops elengi
5	Bamunimaidan(Industrial Estate)		Jamun	Syzygium cumini
6	Chandmari(Near City Bus Stop)	City Road Side	Indian Rubber tree	Ficus elastica Rscto
7	Goswami service		Mast tree	Polyalthia longifolia
8	Silpukhuri bus stop		Mango tree	Mangifera indica
9	Guwahati club Bus Stop		Bakul	Mimusops elengi
10	Fancy Bazar (Near Market Area)	Commercial	Aahat	Ficus religiosa Linn.

11	Kalipur (Sanitary & Marble Shop)		Jack Fruit	Artocarpus
12	Nursery (Near Aluminum Shop)		Kadam	Anthocephalus
13	Adabari (Near bus terminus)		Bakul	Mimusops elengi
14	Jalukbari (Near Gauhati University)	Sensitive	Red Gum	Eucalyptus
15	Jalukbari (Near GU SBI)		Kuros	Derris indica Bennet.
16	Jalukbari (Near Samanay Khetra)		Bakul	Mimusops elengi
17	Basistha (Near Oza Hyundi)	NH 37 Road Side	Jack Fruit	Artocarpus
18	Basistha Chariali (City Bus Stop)		Queens Flower	Lagerstroemia
19	Basistha (Near petrol pump)		Rain tree	Samanea saman
20	Sarusajai (Near game village)		Teok	Tectona grandis Linn.

Fig.-1: Various Road Dust and Tree Bark Sampling Locations at Different Zones of Guwahati

Plant Barks Sample Preparation

Plant barks samples were gently washed with deionized distilled water for near about 3 minutes from removing soil and dust particles followed to the plants. Samples of plants have been dried in the air after washing for 2 weeks at room temperature.¹⁹ All plant samples have been dried oven at 70-80°C as well as it was ground to fine powders by using a domestic mixer grinder¹⁹ and sieved in a 0.2mm sieve. Every sample of the plant has been stored in a plastic bag with clean self-sealing.

1g of dried plant material has been taken in a conical flask (100 ml). Subsequently, 0.5 ml 60% HClO₄, 2.5 ml HNO₃ as well as 0.5 ml H₂SO₄ have been mixed to it. The solution was heated at a low temperature. Increased the heat and digested for 15-20 minutes till white fumes were evolved. Cooled and filtered and made up the final volume to 1000 ml after several washings of filter paper by a small portion of distilled water. The extract was light pink.²⁰

Extract for Deposited Road Dust Samples

The dust samples were digested in triacid mixture (1:2:4; HNO₃, HClO₄ and H₂SO₄), 1g dust sample + 30ml acid mixture heated to dryness, cooled (White residue was obtained) 10 ml of 1:1 HCl + 40 ml distilled water were added to it filtered by Whatman No.40 filter paper volume of the filtrate has been made up to 100ml. The extract was ready to analyze heavy metals Co, Ni, Mn, Cd, Zn, Cu, Cr, Fe, along with Pb.²⁰⁻²²

Sequential Extraction for Chemical Metal Speciation

The Procedure of sequential extraction²³⁻²⁷ is utilized in this speciation. Every chemical fraction of Zn, Cr, Ni, Fe, Cu, Co, Cd and Pb, the in-plant sample is operationally defined as follows:

- F₁ (Exchangeable fraction linked with carbonated stages),
- F₂ (Carbonate bound fraction)
- F₃ (Reducible fraction or fraction connected with oxides of Fe as well as Mn)
- F₄ (Oxidisable fraction bound to organic matter)
- F₅ (Residual or lattice metals).

This process involved:

- (i) extraction with 10ml of MgCl₂ (1.0 M) buffered at pH 7.0 shaking continuously at 300K for 1 hour for obtaining F₁,
- (ii) treating the residue from (1) with 10 ml CH₃COONa (1.0 M) (at pH 5.0 with acetic acid) at 300K for 5hour for extracting F₂ fraction.
- (iii) treating the residue from (2) with 20.0 ml of NH₂OH.HCl (0.04 M) dissolved in acetic acid (25% (v/v)) at 370K and stirring until complete dissolution to get the F₃ fraction.
- (iv) mixing the residue from (3) with 5.0 ml of H₂O₂ (30% (v/v)) and 3.0 ml of HNO₃ (0.02 M) (at pH2.0, adding more HNO₃ if needed) and at 358K heated for 2hours with alternating agitation, cooled at room temperature, after that again mixed with 3.0 ml of HNO₃ (0.02 M) along with 5.0 ml of H₂O₂ (30% (v/v)) (adjusted to pH 2.0 with HNO₃) keeping the solution at 358K for 3hours and stirred, along with cool down and addition of 5.0 ml of CH₃COONH₄ (3.2 M) mixed with HNO₃ (20% (v/v)) diluted to 20ml and continuously stirring for next 30 minutes for obtaining F₄ fraction, and
- (v) digesting the residue from (4) with acid mixture containing H₂SO₄, HNO₃, HCl (4:2:1) ratio for 3 hours until complete dissolution is formed, dilution with 100ml of double distilled water for getting the remaining F₅ fraction.²⁸⁻³⁰ The solubility and bioavailability of metals decreases generally as residual< organic bound< Fe-Mn oxide bound< carbonate bound< exchangeable.³¹

Apparatus and Reagents

Glassware used for extracting process has been firstly washed with 1% HNO₃ (v/v) as well as detergent, washed completely with plain tap water and then distilled water. Immediately after every extraction action, the mixture was centrifuged at 6000 rpm for 1 hour (Remi tools, Mumbai, India). Sequential extractions have been completed with the help of sample (1 gram each) powder along with sieved with a 100mesh sieve. Extractions have been completed in 25ml polypropylene centrifuge tubes, having a mechanical shaker for mixing the solutions as needed. To follow every extraction, the mixture has been centrifuged at 6000rpm for 1 hour, and also the supernatant solution has been separated by pipette.³² The supernatant solution was decanted into polythene plastic bottles and saved for analysis. The residue was cleaned in 10ml-distilled water and centrifuged again. Acid digestion has been performed in glass beakers (borosil). 10% HNO₃ was used for cleaning plastic wares. All of the reagents used were AnalaR quality or even far better.^{1, 33}

The concentrations of heavy metals which include Pb, Cd, Ni, Cu, Mn, Fe, Cr, Co, along with Zn have been estimated by Atomic Absorption Spectrophotometer (Agilent Spectra AAS 220) using Agilent calibration standards for every metal.²⁴ Quantification of metals has been based on calibration curves of regular metals solution. The accuracy of the metallic analysis has been managed by incorporating triplicate samples to come down with analytical blanks as well as batches.³⁴

Environmental Pollution Indices

The environmental contamination level with heavy metals as well as associated hazards have been evaluated by using several established indices.³⁵

- (i) Pi (Pollution index) is defined as:³⁶

$$Pi = C_n / C_{ref}$$

Pollution indices (Pi) indicated the pollution categories

Pi < 1 = Unpolluted

Pi = 1 -2 = Pollution at Low Rate

Pi = 2 -3 = Pollution at Moderate Rate

$P_i > 3$ = Pollution at High Rate

- (ii) following formula defines the ecological risk factor index.

$$Er_i = T_i \times C_n / C_{ref}$$

Where T_i represents the metal's toxic response factor. The specific metals demonstration variable toxicity amounts to humans. According to Hakanson and Soliman the various metal values are Mn-1, Zn-1, Pb-5, Ni-5, Cu-5, Cr-2, and Cd-30^{37,38} for calculating this index.³⁵ There are 5 kinds of pollution that are well-known: > 320 (very high), $Er_i = 160 - 320$ (high) $Er_i = 80 - 160$ (considerable), $Er_i = 40 - 80$ (moderate), and < 40 (low).

- (iii) The potential RI (ecological risk) is described as “the sum of the index of ecological risk factors (Er_i) for metals in a given sample”.^{35,38,39} There are 4 types of index as:³⁷ $RI > 600$ (high), $RI = 300 - 600$ (considerable), $RI = 150 - 300$ (moderate), and $RI < 150$ (low).
- (iv) The Meta analytical analysis describes the correlation between soil heavy metal (HM) content with relative or actual plant heavy metal (HM) uptake. Mobility ratio (MR) is calculated to quantitatively characterize the origin and transfer of the elements.^{40,41} Mobility ratio that expresses the ratio of the plant HM has been up taken concerning HM in soil.⁴²

$$MR = HM_{plant} / HM_{soil}$$

It has been suggested that by calculating MR or ‘Concentration factors CF’ the uptake characteristics of plants are easier to understand. Four categories of the index are distinguished:⁴³ plants enrich these HM ($MR > 1$), indifferent behavior of the plant towards these HM ($MR = 1$) and the plant excludes this HM from uptake ($MR < 1$).

- (v) The Mobility Factor (MF) defines “as the ratio of exchangeable (F_1), carbonate-bound (F_2) and reducible fractions (F_3) to the sum of all fractions”^{44,45}. The MF in percentage is computed as:^{27,46}

$$MF = (F_1 + F_2 + F_3) \times 100 / (\sum F)$$

Here, the sum of every fraction is represented by $\sum F$. Mobility Factor is defined as the measurement for potential mobility of a metal.^{47, 48} When the mobility factor index value is high it shows that specific metal is present in a high mobility state along with high accessibility to biological schemes.^{32, 46, 47}

RESULTS AND DISCUSSION

Heavy Metals in Deposited Road Dust (Root) and Tree Bark

The range of metal concentration, mean values, variation coefficient with geochemical background values for deposited road dust and tree bark samples of five different zones are presented in Table-2 and Table-3. The mean concentration of heavy metals in road dust followed the order as $Cd < Co < Pb < Cr < Cu < Ni < Zn < Mn < Fe$ while the mean heavy metal concentration in tree bark samples may be organized as $Cr < Cd < Ni < Cu < Co < Pb < Mn < Zn < Fe$. The variation of mean concentrations of heavy metals for both road dust and tree bark is shown in Fig.-2 excepting the Iron concentration as it was abruptly high in both cases. Among the 9 elements studied, the mean concentration of Fe, Mn and Zn were considerably higher, whereas lower concentration was observed for Co and Cd for both road dust and tree bark samples in five different zones. Soliman also reported a similar trend of heavy metal content in sediments.³⁸

In the present study, the mean values of Ni and Zn in road dust exceed the geochemical background values (4 times on average) while Cu exceeded two times (Table-2). Though the presence of Cd in road dust was least in the order but it appeared considerably high compared to the geochemical background values and Pb content was marginally high. The other metals Fe, Mn, Co and Cr were much lower than the geochemical background values. The mean concentration of Cu, Cd and Zn exceeded the maximum concentration ($Cu - 100$, $Cd - 3$ and $Zn - 300 \mu g g^{-1}$ dry soil) for road dust collected from city roadside and national highway zone. Ni exceeded the maximum concentration of $50 \mu g g^{-1}$ in dry soil¹⁷ for all the zones. It may be due to the high vehicular traffic which resembles the studies Ferguson, who reported that a higher concentration trend has been discovered on streets wherever traffic was more likely to undergo stop-start.⁴⁹ Table-2 indicates that the maximum concentration of Pb was well below the maximum geochemical background values $100 \mu g g^{-1}$ dry soil and it may be due to the introduction of unleaded petrol.⁵⁰

Fig.-2 : Variation of Mean Concentration of Heavy Metals in Deposited Road Dust and Tree Bark Samples

In the case of tree bark, most of the metals Fe, Mn, Co, Ni, and Cd were much lower in comparison to the geochemical background values except Zn (Table-3). The maximum concentration of almost all the metals was within the trigger concentration (Zn-130, Ni-20, Cu-50, Pb-100, and Cd-3, $\mu\text{g g}^{-1}$ in air-dried soil.⁵¹ The lowest heavy metal content appeared in most road dust samples for sensitive zone and the highest appeared in the National Highway -37 zone (particularly Mn, Cu, Pb, Cd, Zn and Cr). A similar trend was observed for tree bark also and the dominant metal was Fe, Mn, Co, Cu, Zn and Cd for the national highway zone. It has been observed that there was a high variation among the studied metals for both road dust and tree bark samples in five different zones. The variation coefficient (VC) Study in road dust (Table-3) displayed that Cd, Zn, Cu, and Mn, was in $\text{VC} > 50$ (a high variation level) while Pb and Cr were in the order $40 > \text{VC} > 20$ (a minimum variation level) and the lowest variation was for Ni as well as Co ($\text{VC} < 20$). In the case of Tree bark, the highest variation appeared for Mn and Ni while Cu and Zn showed the minimum variation level. The variation was lowest in tree bark samples for Co, Pb and Cd (Table-3). Martin et al. described that the higher the value of VC indicates the high anthropogenic influence.⁵²

Table-2: Contents of Heavy Metal in Deposited Street Dust in Guwahati ($\mu\text{g g}^{-1}$)

Metals	Range	Mean	Variation Coefficient (VC) (%)	Geochemical Background ^{a,b}
Mn	36.1 – 818.8	279.1	112	495 ^a
Fe	17211 - 41201	27174.4	41	37400 ^a
Co	6.6 – 10.1	8.5	16	10 ^b
Ni	198.2 – 220.4	212.3	5	50 ^b
Cu	5.6 – 124.4	63.8	68	20 ^b
Zn	43 – 821.9	229.2	145	50 ^b
Pb	11.7 – 29.1	19.9	32	20 ^b
Cd	0.7 – 7.9	4.0	85	1 ^b
Cr	19.6 – 42.2	29.5	31	50 ^b

Table-3: Contents of Heavy Metal in Roadside Tree Bark in Guwahati ($\mu\text{g g}^{-1}$)

Metals	Range	Mean	Variation Coefficient (VC) (%)	Geochemical Background ^{a,b}
Mn	14.3 -67.3	37.6	54	495 ^a
Fe	138.3 – 435.4	308.6	48	37400 ^a
Co	6.5 – 9.0	7.9	14	10 ^b
Ni	0.1 – 2.8	1.3	93	50 ^b
Cu	6.2 – 10.5	7.7	21	20 ^b
Zn	41.1 – 105.2	79.5	30	50 ^b
Pb	13.9 – 21.8	17.3	17	20 ^b
Cd	0.7 – 1.1	0.8	20	1 ^b
Cr	BDL	BDL	-	50 ^b

Geochemical Background^{a,b} 38, 50

Heavy metal in street dust is mainly initiated from multiple types of human activities such as tears and wear of vehicles, exhaust emissions, fuel ingestion, as well as industrial activity.^{53,54} In the whole world, Cu is at the 3rd place for the utilization.⁵⁵ Cu is commonly utilized in vehicle oils.⁵⁶ Cu may also come to the roadside environment as a consequence of rusting of car parts such as metals etc. and wear of motor oil pumps^{35,57} along with tear and wear of engine.^{56,58} Cd and Zn are connected with the wear of tire along with Zn particularly resulted in spills on the surface of road.⁵⁹ Cd is also significantly used in the production of Ni/Cd rechargeable batteries.

Zn can disrupt the activity of soils, as it adversely influences the activity of earthworms and microorganisms, therefore retarding the description of organic and the natural matter is important³². The mobility of Cr is dependent upon sorption soil's attributes, such as clay material, organic material as well as the presence of iron oxide. The leachability of Cr is directly proportional to soil pH⁶⁰. Ni is an element that happens on the planet just at really low levels and it is vital in doses that are little though it is harmful if exceeds the tolerance limit.⁶⁰

This research work described the presence of heavy metals and their toxicity to humans as well as plants. Ingestion along with Inhalation is the 2 major exposure routes to toxic elements. It has been reported that Pb gathers in the human body such as the brain that can lead to death or poisoning. Lead also affects the central nervous system, kidneys, gastrointestinal tract, IQ, mental deterioration.⁶⁰ Generally, plants cannot accumulate or absorb lead, but there is a high risk of lead-contaminated dust or soil deposits on the plants instead of taking lead through plants.⁶⁰

Cd is quite bio-resistant, once assimilated by an organism is still resident for numerous years. The main risk to human health because of Cd toxicity is a chronic buildup of the kidneys triggering kidney dysfunction, neoplastic changes as well as hypertension.³⁵ The toxicity of Ni and Cu is minor though humans are susceptible to the bioaccumulation of these metals assimilated into the entire body through the breathing system.^{35,61} Cu is a vital micronutrient essential in the development of both animals as well as plants. In humans, it can help in the generation of blood hemoglobin. Cu is particularly crucial in water regulation, disease resistance along seed generation in Plants.⁶⁰ Cu is considered an essential element, but excessive doses may also cause intestinal and stomach irritation, kidney and liver damage, anemia.⁶⁰ Ni is not recognized for accumulating in animals or plants but Ni toxicity can cause various types of cancer in human bodies. Several of the signs related to ailments from extra nickel coverage such as cough, giddiness, headache, virtual disturbances, stomach upset, vomiting and nausea.⁶⁰ Mn deficiency might result in diabetes mellitus, epilepsy, and osteoporosis, while neurological toxicity is related to excessive manganese.⁶⁰ Zn is among the important heavy metals. Due to its deficiency ensuing from mal-absorption, alcoholism, and diet might result in dwarfism, dermatitis and hypogonadism whereas unnecessary awareness within the body might result in nausea, electrolyte imbalance and anemia.^{60, 62}

Assessment of Bioavailability of Heavy Metals in Tree Barks

The metal contamination and its potential hazard were assessed based on the total metal concentration obtained by total acid digestion of the plant materials. All the studied heavy metals may not be bioavailable, thus the tree bark samples have been sequentially extracted to measure the chemical metal speciation and as a consequence give an indication of bioavailability and mobility of heavy metals.

The metal speciation in tree bark samples (Table-4) showed that the Fe (43%) and Mn (34%) was mostly connected with Fe-Mn oxide fraction respected through the least easily available fraction organic matter or sulphide fraction (Fe-21%, Mn-26%) and the rest being related with exchangeable, residual as well as fraction of organic matter.

The least available residual fraction also accounts for about 52% of total Co content in the tree bark samples. The Ni (61%) and Pb(47%) were found to be only in the readily available exchangeable fractions. The fractional profile showed that Cu (44%), Zn (63%) and Cd (30%) had the highest percentage in the least available organic matter or sulphide fraction. The metal speciation study in tree bark samples clearly showed that Ni and Pb may be the most bioavailable metal followed by Cu, Zn, Cd and Mn under appropriate environmental conditions. Figure-3(a to f) showed the speciation of metals in tree bark into five different chemical fractions.

Table-4: Statistical Summary of Heavy Metal Content in Various Fractions of Tree Bark concerning all 20 Locations in Guwahati ($\mu\text{g g}^{-1}$)

	Fractions	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
Min	Exchangeable	10.9	44.5	2.4	69.4	3	0	114.4	0.1
Max		18.5	95.6	4.4	137.8	44.5	0	118.6	0.5
Mean		14.3	65.3	3.5	104.4	12.7	0.0	117.0	0.3
SD		3.3	24.2	0.8	26.5	17.8	0.0	1.6	0.1
Min	Carbonate	2.0	17	4.5	16.0	8.6	25.8	25.0	0.1
Max		5.1	64.6	9.3	32	14.6	87.3	34.5	1.6
Mean		3.6	42.7	7.4	22.8	11.6	50.2	28.8	0.7
SD		1.5	21.0	2.1	6.4	2.7	22.8	3.9	0.6
Min	Reducible	15.4	298.6	2.0	8.9	12.9	193.5	23.6	0.2
Max		35.6	355.8	25	14.6	14.4	979	35.6	1.0
Mean		23.2	340.2	7.3	11.4	13.6	451.5	26.8	0.5
SD		7.6	23.8	9.9	2.3	0.6	320.6	4.9	0.4
Min	Organic Matter	13.7	80.5	2.2	5.2	18.7	86.3	22.3	0.55
Max		22.1	341.9	16	34	60.5	1926.5	59.8	1.6
Mean		17.5	166.6	6.0	15.1	40.6	893.2	39.4	0.9
SD		3.2	112.1	5.7	13.8	19.0	812.0	15.5	0.4
Min	Residual	2.5	13.4	3.4	2.15	10.3	8.2	34.7	0.4
Max		13.9	238.4	44	73	20.1	34.2	40.5	0.8
Mean		9.9	178.4	26.2	16.9	14.6	17.1	37.8	0.6
SD		4.4	93.9	20.2	31.4	4.3	10.2	2.9	0.2

Environmental Pollution Indices

The pollution index (Pi) study (Table-5) showed that the national highway roadside zone was indexed as high pollution ($P_i > 3$) in terms of heavy metals Ni, Cd, Zn and Cu while low pollution ($P_i = 1-2$) concerning Pb and Mn. According to the ecological risk study (Eri), Table-5 revealed that a low (< 40) pollution index has been obtained for Mn, Zn, Ni, Cu, Pb and Cr for all the samples. In Cd content case, the risk was considerable ($E_{ri} = 80 - 160$) and it was also in the national highway roadside zone.

The potential ecological risk (RI) was ranged from 63.8 – 317.1 where the three zones (Industrial, Commercial and Sensitive) were under the low potential ecological risk category ($RI < 150$) while the City roadside zone under the moderate risk category ($RI = 150 - 200$). The highest level ($RI = 317.1$) was obtained in the national highway roadside zone and felt under considerable potential ecological risk category ($RI = 300 - 600$).

The Meta analytical study (Table-5) showed that the mean values of mobility ratio were excluded from the uptake or enrichment of any heavy metals as $MR < 1$. The mobility factor (MF) index study showed that among the seven-studied metal the highest mobility appeared concerning Ni while lowest mobility towards Co. The MF index was in order $Co < Cu < Zn < Cd < Mn < Pb < Ni$. The heavy metal with high MF values indicates that the metal is highly labile as well as bioavailable.⁴⁴

Table-5: Statistical Summary of Various Environmental Indices in Street Dust and Tree Bark samples concerning all 20 Locations in Guwahati ($\mu\text{g g}^{-1}$)

	Indices	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd	Cr
Min	Pi	0.07	0.46	0.66	4.1	0.28	2	0.58	1.9	0.39
Max		1.65	1.1	1	4.4	6.2	16.4	1.5	7.9	0.84
Mean		0.6	0.7	0.8	4.2	3.2	4.6	1.0	4.0	0.6
SD		0.6	0.3	0.1	0.2	2.1	6.6	0.3	3.4	0.2
Min	ERi	0.07	0	0	19.8	1.4	0.86	2.9	21	0.78

Max		1.65	0	0	22	31.1	16.4	7.3	237	1.7
Mean		0.6	0.0	0.0	21.2	15.9	4.6	5.0	121.2	1.2
SD		0.6	0.0	0.0	1.0	10.8	6.6	1.6	102.9	0.4
Min	MR	0.082	0.008	0.64	0.0	0.08	0.099	0.549	0.092	-
Max		0.65	0.017	1.21	0.013	1.35	2.44	1.46	1.142	-
Mean		0.26	0.011	0.95	0.006	0.35	0.97	0.96	0.38	-
SD		0.24	0.004	0.21	0.006	0.56	0.89	0.39	0.43	-
Min	MF of	53.1	-	18.2	49.6	31.4	12.9	64.1	32.6	-
Max		67.7	-	62.8	95.3	50.5	89.8	74.4	66.3	-
Mean		60.2	-	39.0	83.5	40.0	42.9	69.4	46.8	-
SD		5.6	-	16.6	19.5	8.2	33.8	4.8	16.2	-

Fig.-3a: Fractional Distribution of Mn in Tree Bark

Fig.-3b: Fractional Distribution of Co in Tree Bark

Fig.-3c: Fractional Distribution of Ni in Tree Bark

Fig.-3d: Fractional Distribution of Cu in Tree Bark

Fig.-3e: Fractional Distribution of Zn in Tree Bark

Fig.-3f: Fractional Distribution of Pb in Tree Bark

CONCLUSION

The present work comprehensively evaluated the total heavy metal content, as well as sequential extraction study and various environmental indices for Pb, Cr, Cd, Cu, Zn, Co, Mn, along with Fe, in different roadside, deposited road dust and adjacent tree bark belonging to five different types of zones in Guwahati. In deposited road dust, the concentration of heavy metal particularly Cd, Zn, Cu, and Ni exceeded not only geochemical background values but also the maximum concentration level in uncontaminated dry soil. But in the case of roadside tree bark, all the nine studied metals were well below the geochemical background values except Zn content, which was on a little higher side. The fractional profile in tree bark showed that Ni and Pb were mostly associated with exchangeable fractions while Mn bound to a reducible fraction in considerable amounts. Zn, Cu, and Cd were mostly connected with organic matter/ sulphide fraction. In the present work higher percentage of metals in tree bark were mostly bound to exchangeable, carbonate as well as organic matter fractions. This can be a matter of concern that the metals Co, Ni, Zn, Cu, Mn, Cd, and Pb can be discharged to the surroundings under suitable environmental conditions as well as may alter the ecological equilibrium. Heavy metal contamination levels based on environmental indices indicated that Ni, Cd, Cu and Zn were in the high pollution category while Pb and Mn were low concerning pollution index. The potential ecological risk study categorized the five different zones as three zones (Industrial, Commercial and Sensitive) were under low potential ecological risk while City roadside zone under moderate risk. The national highway roadside zone was categorized under considerable potential ecological risk. Since Guwahati is free from any major industries, thus present study indicates that the anthropogenic factors (vehicular emissions, motor traffic-related activities) may be predominately responsible for the contamination of road dust as well as roadside tree bark with heavy metals. Additionally, the environmental significance of the results as well as the pollution level of other metals such as Hg, Se needs to be further investigated.

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