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## Assessment of polycyclic aromatic hydrocarbons and heavy metals pollution in soils of Guwahati city, Assam, India

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Soil pollution in Guwahati city, Assam, India has become a major concern since the last few decades. To study the impact of automobile and industrial emission, distribution patterns of 16 different polycyclic aromatic hydrocarbons (PAHs) and eight heavy metals were investigated in the soil samples collected from 15 different sites. Higher concentration of total PAHs and heavy metals was found in the industrial areas compared to the high traffic areas. Differences in the pollutants observed between the polluted and non-polluted sites, endorse that anthropogenic activities are the major cause of soil contamination.

**Keywords:** Automobile and industrial emission, heavy metals, polycyclic aromatic hydrocarbons, soil pollution.

PROTECTION of soil is presently a worldwide concern. Urbanization, industrialization and population increase over the last few decades have enhanced the release of toxic organic pollutants, viz. polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) into the environment due to various anthropogenic activities such as fuel burning, industrial emissions, corrosion of metallic particles, etc.<sup>1</sup>. Soil systems are the long-term storehouse of such pollutants and are considered to be a steady index of the state of environmental pollution<sup>2</sup>. The primary input of such organic pollutants into the soil surface is by air-to-surface precipitation<sup>3</sup> and it persists in the toplayer of the soil<sup>4</sup>. Because of the toxicity, exposure to such pollutants in the environment is detrimental to human health and so has become the focus of much attention<sup>5,6</sup>.

Many HMs are naturally occurring; however, some are hazardous, particularly in high concentrations in human and plant cells. Sakagami *et al.*<sup>7</sup> have outlined

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the relationship between trace metal concentration in roadside soil and that in the dust falls. The soil has a tendency to accumulate HMs on a relatively long-term basis, since many metals in the soil are mobile. HMs like Pb from leaded gasoline, Cu, Zn and Cd from car components, lubricants, and industrial emissions are major pollutants of the roadside domain<sup>8,9</sup>. Cd, Cr, Cu, Fe, Mn, Pb and Zn have been shown to be associated with ambient particles released by roadside dust, and can cause the building and spread of inflammatory mediators by the respiratory tract epithelium<sup>10</sup>.

PAHs are among the organic pollutants that are toxic and ubiquitous in the environment. The United States Environmental Protection Agency (US EPA) has selected 16 PAHs as the most important ones to be analysed in different environmental matrices because of their toxicity<sup>11</sup>. PAHs have often been found to coexist with heavy metals due to similar pollution origin<sup>12</sup>. Motor vehicle emissions are a feasible source for both the pollutants. They preferentially accumulate in the soil because of their hydrophobic nature and stable chemical structure<sup>13</sup>. Many studies on the distribution, transfer and sources of PAHs have been made in the last 50 years and their strong conflicting biological effects have been documented<sup>14,15</sup>.

In recent times, studies are being conducted on HMs and PAHs in urban/rural soil, including those contributed by automobiles along transport routes<sup>16</sup>. The release of such pollutants into the environment is related to environmental management problems of transport, which varies across time, location, intensity of human activities and traffic volume, mobility and bioavailability<sup>17</sup>.

The present study was undertaken to assess USEPA's 16 priority PAHs and HMs in samples collected from the soil of traffic-loaded and industrial areas of Guwahati city, Assam, India. The outcome of this study may provide guidelines for further studies on soil contamination in the region.

Guwahati city, the gateway to North East India, is situated in the banks of the Brahmaputra River and close to the foothills of the Shillong plateau (26°10'0"N and 92°40′0″E). Over the last decade, the city has witnessed an enormous increase of vehicular growth on the roads. The core or the 'city centre' lies in the areas of Pan bazar, Paltan bazar, Fancy Bazaar and Chandmari, with many tourism and leisure activities. The north-southeast Guwahati-Shillong (GS) road corridor and Ganeshguri, situated in the southern part of Guwahati city are other sub-centres of high traffic during peak hours. The western corridor towards Kamakhya, Jalukbari and Lokpriya Gopinath Bordoloi International Airport (LGBI), and the eastern corridor towards Noonmati and Narengi, with an oil refinery are also some other areas with heavy traffic. A national highway, NH-37, which runs along the southern part of the city and links the southern to the western corridor, in Jalukbari, is currently one of the areas of rapid development with huge traffic. Some of the key

sources of pollution at these sites include illegal dumping of raw sewage into public areas, road traffic, industrial quarters, oil refinery and vehicle maintenance workshops.

Soil samples were collected from 15 sites of Guwahati city. Figure 1 shows a map of Guwahati city obtained from\_Assam and Nagaland Geo-spatial Data Centre (GDC), Survey of India. Table 1 provides a brief description of the sampling sites. Collections were made in the pre-monsoon period of 2014. Triplicate samples were taken from the surface soil. They were dried at room temperature and labelled, followed by grinding and sieving to obtain homogenized samples.

PAHs were extracted according to the method of US EPA<sup>18</sup>. Soil samples (5.0 g) were subjected to Soxhlet extraction for 16 h with dichloromethane (DCM). Extracts were concentrated using a rotary vacuum evaporator (Buchi R-3) and solvent exchanged to 5 ml cyclohexane. Column chromatography was used to clean the extracts containing PAHs using DCM as eluent through silica gel (100-200 mesh). The concentrated extract in cyclohexane was passed through a pre-eluted column with 25 ml n-pentane and speed of the eluent was adjusted to approximately 2 ml/min. The collected fractions were concentrated in a rotary vacuum evaporated at low temperature followed by solvent exchange with acetonitrile and its volume was made up to 5 ml. The final extracts were analysed by high performance liquid chromatography (HPLC) for identification and quantification of PAHs comparing with known concentration of external standard. The HPLC system (Waters, USA), consisted of Waters-515 binary pump, Rheodyne injector-7725 with 20  $\mu$ l loop, Waters column C-18 (250 × 4 mm, dp: 5  $\mu$ m) and Waters UV detector-2487 at 254 nm. Elution was performed using acetonitrile: water (70:30) solvent system at a flow rate of 1.5 ml min<sup>-1</sup> with a run time of 50 min. Data acquisition and processing were carried out using Empower 2 chromatography manager software (Waters, USA).

One gram of each of the collected soil samples was digested by gentle heating, initially with 10 ml nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>) [4:1 v/v] (until no brown fumes appeared). The final volume was made up to 10 ml with 1% HNO<sub>3</sub>. Analyses of the heavy metals (Ni, Zn, Cr, Mn, Cd, Cu, Fe and Pb) were carried out on an atomic absorption spectrophotometer (AA-7000 SHIMADZU) using acetylene gas as fuel. Measurements were made using an external standard calibration graph. Each analysis was done in triplicate, including blanks. Analysis was done using the protocol outlined by the American Public Health Association<sup>19</sup>.

Statistical analyses for metal concentrations were performed by Pearson correlation (parametric) analysis using IBM SPSS (statistics 20) software. Principal component analysis (PCA) was performed in Paleontological Statistics (PAST) (version 3.04) software using correlation

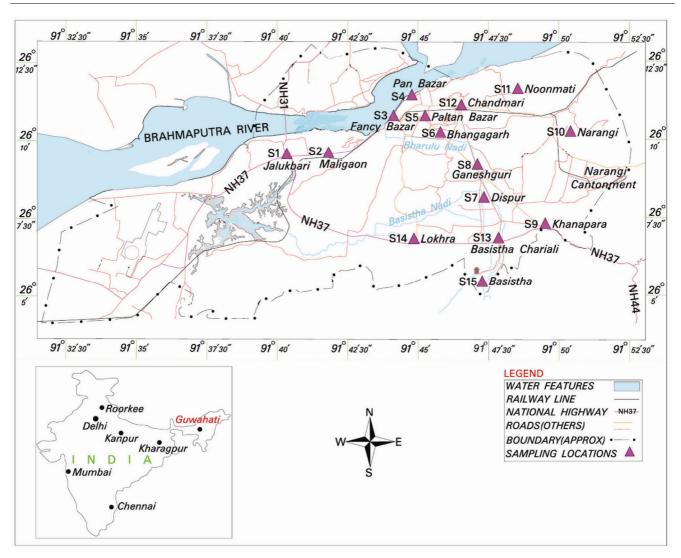


Figure 1. Map of Guwahati city, Assam, India showing sampling locations.

Table 1. Description of sampling sites in Guwahati city, Assam, India

Site nos	Sampling site	Traffic load	Population load	Land used	Geographical location		
S-1	Jalukbari	High	Dense	TA, CA	26°9′26.88″N and 91°40′22.22″E		
S-2	Maligaon	Medium	Dense	RA, CA	26°9'32.59"N and 91°41'45.66"E		
S-3	Fancy bazaar	Medium	Dense	TA, CA, RA	26°11'3.12"N and 91°44'18.79"E		
S-4	Panbazar	Medium	Dense	CA, TA	26°11′17.00″N and 91°44′35.75″E		
S-5	Paltanbazar	High	Dense	TA, CA	26°10'43.92"N and 91°45'5.31"E		
S-6	Bhangagarh	Medium	Dense	CA, RA	26°10′1.75"N and 91°45′58.63"E		
S-7	Dispur	High	Dense	CA, RA, TA	26°8′29.24"N and 91°47′43.50"E		
S-8	Ganeshguri	High	Dense	CA, RA, TA	26°8'47.39"N and 91°47'21.27"E		
S-9	Khanapara	High	Dense	CA	26°7′13.05"N and 91°49′19.03"E		
S-10	Narengi	Low	Sparse	IA, TA, RA	26°10′14.76″N and 91°49′44.63″E		
S-11	Noonmati	Low	Sparse	IA, TA, RA	26°11′53.77"N and 91°47′58.73"E		
S-12	Chandmari	Medium	Dense	CA, RA	26°11′0.36"N and 91°46′26.68"E		
S-13	Basistha chariali	High	Dense	CA, RA, TA	26°6'43.79"N and 91°47'52.58"E		
S-14	Lokhra	Medium	Dense	CA, RA	26°6'42.07"N and 91°44'58.12"E		
S-15	Basistha (control)	Low	Sparse	RA	26°5′23.57"N and 91°46′38.59"E		

TA, Traffic area; CA, Commercial area; RA, Residential area; IA, Industrial area.

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PAHs	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Naph	37.4	24.2	41.6	12.1	52.8	29.4	21.8	13.5	80.8	106.2	76.8	20.5	37.5	11.2	7.1
Acy	13.5	18.2	11.1	6.4	15.6	4.7	17.4	3.6	16.8	28.8	21.2	6.0	19.6	4.8	3.1
Acen	21.2	10.7	11.5	2.3	11.2	9.8	ND	ND	14.4	71.0	21.2	10.2	30.6	10.6	ND
Flu	13.8	12.6	12.2	12.2	4.8	1.7	2.0	1.4	7.2	14 .4	13.6	31.6	16.9	3.8	0.9
Phen	9.2	9.2	7.7	5.2	9.6	4.8	ND	4.8	6.2	8.2	15.6	4.8	5.8	2.6	ND
Anth	27.4	21.6	20.2	11.8	13.6	9.4	19.6	15.0	19.4	51.6	23.8	17.5	72.4	11.9	10.7
Flan	118.8	55.6	14.6	1.6	3.7	ND	11.8	1.2	12.6	104	130.8	2.7	5.3	4.3	3.2
Pyr	2.2	11.2	1.7	1.1	6.6	2.4	1.5	0.9	3.2	13.6	16.6	ND	1.5	0.8	0.8
BaA	20.0	12.2	19.2	ND	26.7	8.2	13.4	11.6	8.2	28.8	59.6	11.2	16.4	7.8	5.2
Chry	11.2	2.2	5.0	1.3	16.6	2.1	ND	0.2	19.6	67.4	58.8	2.4	15.1	1.7	ND
BbF	9.6	14.3	14.4	11.1	22.1	8.6	4.7	11.0	10.6	25.8	23.6	5.4	10.6	15.5	3.6
BkF	29.8	15.0	14.4	5.4	25.2	7.1	29.2	15.2	16.9	58.8	46.6	11.2	40.8	14.7	0.9
BaP	48.8	20.8	14.6	10.0	15.8	8.1	32.1	73.8	20.6	68.8	47.2	21.6	102.4	10.8	5.3
IP	35.2	10.5	11.3	ND	2.1	0.7	12.2	4.6	0.5	31.7	15.8	17.2	21.0	ND	1.9
DBA	17.6	4.6	9.6	1.6	7.2	0.8	12.0	7.9	15.7	30.6	25.2	0.2	15.8	7.3	ND
BgP	20.7	13.5	22.5	10.8	5.2	9.8	16.1	ND	25.9	32.6	31.6	14.7	23.8	10.1	ND
∑PAHs	436.4	287.2	231.6	92.9	238.8	107.6	193.8	164.7	278.6	742.3	628	177.2	435.5	117.9	42.7

Naph, Naphthalene; Acy, Acenaphthylene; Acen, Acenaphthene; Flu, Fluorene; Phen, Phenanthrene; Anth, Anthracene; Flan, Fluoranthene; Pyr, Pyrene; BaA, Benzo(a)anthracene; Chry, Chrysene; BbF, Benzo(b)fluoranthene; BkF, Benzo(k)fluoranthene; BaP, Benzo(a)pyrene; IP, Indeno(1,2,3-cd)pyrene; DBA, Dibenz(a,h)anthracene; BgP, Benzo(g,h,i)perylene;  $\Sigma$ PAHs, Total PAHs.

Table 3. Classification of soil contamination by PAHs

Class	Concentration of 16 PAHs (µg/g)
Not contaminated Weakly contaminated Contaminated	<200 200–600 600–1000
Heavily contaminated	>1000

method. Clustering of the sample sites in PCA analysis was carried out using var-cover method.

The 16 PAHs have been analysed to assess anthropogenic pollution levels in the soil of Guwahati city. The concentration of total PAHs was found to be in the range 42.7-742.3 μg/g (Table 2). According to the classification of Maliszewska-Kordybach<sup>20</sup> as summarized in Table 3, most of the sites are considered to be contaminated. Sampling sites S-10 and S-11, which fall within an oil refinery and a traffic-loaded area, were found to contain substantially higher concentration of total PAHs (742.3 and 628 µg/g respectively) and are considered as highly contaminated, according to the classification in Table 3. The other sites that were within the traffic and land-use areas were found to be weakly contaminated and were in the range 436.4–231.6 µg/g. S-1 (Jalukbari) which is one of the areas of rapid development with huge traffic, and links the southern and western corridors of the city, and S-13 (Basistha chariali) which links the city with the NH-37, contain significantly higher concentration of total PAHs (436.4 and 435.5 µg/g respectively) among all the sites (except the industrial area). The high concentration of PAHs in the industrial area compared to the high traffic areas might be due to release of PAHs during industrial emission along with traffic exhausts<sup>21</sup>. Sites S-4, S-6, S-7, S-8, S-12 and S-14 which showed total concentration of PAHs lower than 200  $\mu$ g/g, were not considered as contaminated<sup>20</sup>. However, relatively low concentration (42.7  $\mu$ g/g) of PAHs in sample site S-15 (control) implies that the industrial area followed by few of the heavy traffic-loaded areas are the most affected sites, presumably by industrial and vehicular emission ((S-10, S-11) > (S-1, S13) > (S-2, S-3, S-5, S-9)).

Among the PAHs, naphthalene, acenaphthylene, anthracene, fluoranthene, chrysene and benzo(a)pyrene were found in higher concentration. These compounds, emitted from incomplete combustion, get adsorbed to particles that are suspended in the air and are deposited in the soil and dust near the roadside<sup>21</sup>. According to Yang et al.<sup>22</sup>, such low molecular weight PAHs are considered to cause significant acute toxicity. Thus, varied environmental conditions at different locations in terms of physico-chemical properties of PAHs could explain the effect on environment and also that industrial effluents are the major source of PAHs contamination followed by vehicular emission in traffic-loaded area.

The consequences of heavy metals introduced by human activities into the ecosystem have recently become the subject of widespread concern, because of toxicity beyond tolerable limits<sup>23</sup>. In the present study Cd, Cu, Fe, Zn, Cr, Mn, Ni and Pb were found to be higher in all the sampling sites compared to the non-polluted site (S-15).

Figure 2 shows the average concentration of heavy metals in the soil from various sampling locations. Available Zn concentration (Figure 2 a) was found to be above the desired limit of  $0.6-2.3 \mu g/g$  in high traffic areas (S-1 = 3.73, S-5 = 4.0, S-4 = 2.34, S-9 = 2.97, S-10 = 6.09, S-11 = 3.88 and S-13 = 2.92  $\mu g/g$ ), but was found to be within the permissible limit of  $0.6-10 \mu g/g$ . Samples of

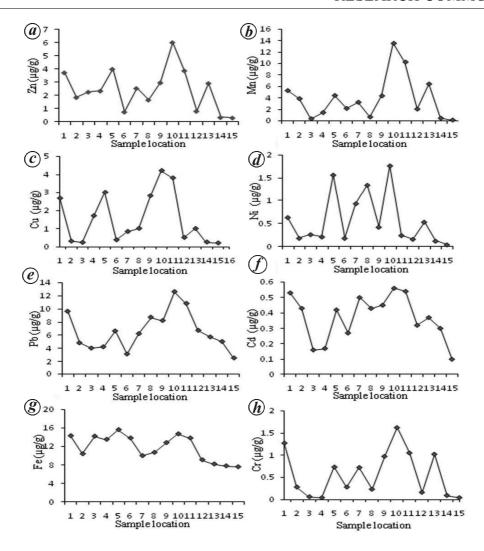


Figure 2. Total concentration of heavy metals  $(\mu g/g)$  in soil samples of Guwahati city.

**Table 4.** Descriptive statistics of the concentration of heavy metals  $(\mu g/g)$ 

Metals	Minimum	Maximum	Mean	±SD
Zn	0.30	6.10	2.42	1.55
Ni	0.04	1.76	0.57	0.55
Cr	0.04	1.65	0.57	0.50
Mn	0.11	13.52	3.62	3.84
Cd	0.08	0.57	0.37	0.14
Cu	0.20	4.22	1.58	1.43
Fe	7.60	15.60	11.77	2.71
Pb	2.47	12.62	6.58	2.84

S-10 showed a high level of Zn concentration compared to other sites; this could be due to emission by the oil industry. However, since no major industry exists in the sites S-1, S-5, S-4, S-9 and S-13, the source of Zn is presumably the contribution of motor vehicles during high traffic load. In contrast, compared to all the sites, low concentration of Zn ( $<0.6 \,\mu g/g$ ) in the control site indicates that it is a contamination-free area.

Mn concentration (Figure 2 *b*) was observed to have a variable distribution like Zn. Concentration of Mn in soils of S-3 (0.35  $\mu$ g/g), S-4 (1.43  $\mu$ g/g), S-6 (2.15  $\mu$ g/g), S-8 (0.65  $\mu$ g/g), S-12 (2.04  $\mu$ g/g) and S-14 (0.43  $\mu$ g/g) was below the prescribed limit (4–10 ppm). In comparison, the soils of S-1, S-5, S-9, S-13 with concentrations of 5.26; 4.41; 4.34 and 6.42  $\mu$ g/g respectively, were within the permissible limit. However, in S-10 and S-11, contamination of Mn was at a higher level, which may be due to the release of the industrial effluents.

The vehicles plying on the road can emit heavy metals into the air, especially Cu. Thus, traffic density of a site can influence the amount of Cu deposited<sup>24</sup>. Available Cu and Ni concentrations were within the maximum permissible limits of 0.2–5 and 0.2–2  $\mu$ g/g respectively (Figure 2 c and d). However, the industrial areas contained moderately high Cu concentration (i.e. 4.2 and 3.8  $\mu$ g/g). Likewise, Cr concentration in S-1, S-10, S-11 and S-13 (1.62, 1.05, 1.27 and 1.02  $\mu$ g/g respectively) was above the permissible limits of 1.0  $\mu$ g/g, whereas other

Pb

		Table 3.	Correlation harr matrix of metal content in son samples						
Metals	Zn	Ni	Cr	Mn	Cd	Cu	Fe	Pb	
Zn	1.000	0.678	0.867	0.808	0.672	0.877	0.663	0.774	
Ni		1.000	0.550	0.465	0.566	0.579	0.401	0.601	
Cr			1.000	0.812	0.798	0.787	0.411	0.804	
Mn				1.000	0.650	0.702	0.375	0.725	
Cd					1.000	0.634	0.288	0.835	
Cu						1.000	0.676	0.792	
Fe							1.000	0.403	

**Table 5.** Correlation half matrix of metal content in soil samples

All correlations are highly significant at P < 0.01

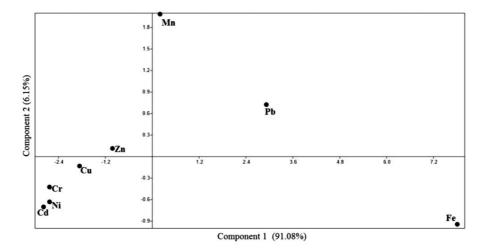


Figure 3. Principal component analysis based on correlation for metal concentration.

traffic areas were within this limit (Figure 2 h). The concentrations of other heavy metals (viz. Pb, Cd and Fe, Figure 2 e-g respectively) were found within the permissible limit (5.2-10, 0.01-0.5 and 2.5-20 µg/g respectively)<sup>25</sup>. Pb deposition in particular, is greatly influenced by vehicular emissions. Pb concentration in case of S-1, S-5 and S-8 being more predominant, could be attributed to heavy traffic on the route, while in the case of S-10 and S-11, it may be due to proximity of the industrial area. Thus greater metal contamination in trafficloaded areas and industrial areas must be the result of vehicular emission and industrial effluent respectively.

Table 4 provides the descriptive statistics (minimum, maximum, mean and standard deviation) of concentration of metals of the various sites.

In order to establish inter-element relationships, correlation coefficients of heavy metal concentrations present in the soil samples were calculated. In Table 5, Pearson correlation using the metal concentration has shown significant positive correlation (P < 0.01) between Zn and Cr (r = 0.867) as well as Zn and Cu (r = 0.877), suggesting that these metals in the street dust may have a common source of pollution. Significant positive correlation (P < 0.01) was also observed between Zn and Mn (r = 0.808), Zn and Pb (r = 0.774) as well as Zn and Fe

(r = 0.663). It might be because Zn is mobile in nature. PCA was conducted based on the inter-element correlation (Figure 3). Distinct clustering of Zn with Cr and Cu in Figure 3, suggests that the source of metal contamination is similar, while Fe, Pb and Mn which are distantly related propose a different origin of metal contamination.

1.000

When the sample sites were compared based on their PAHs and heavy metals concentration, results of PCA indicate that 15 sites can be extracted into two components with high variance (75.15% and 16.30% respectively). PCA plot (Figure 4) reveals that S10 and S11 (group-I), which are in the industrial areas and highly contaminated, are grouped together in a single quadrant; whereas S13 which lies within the same quadrant, signifies considerable contamination rate in the site. The rate of contamination in sites S1, S5 and S9 (group-II), which are clustered separately from the industrial areas in a single quadrant suggests a difference in the rate of soil pollution. Contamination observed in different sites S3, S6 and S4 (group-III) was significantly the same and comes under one quadrant which differs from that of group-I and group-II. Also, sites S2, S7, S8, S12 and S14 (group-IV) are clustered in separate quadrants, denoting identical rate of contamination among the sites. Thus the relationship

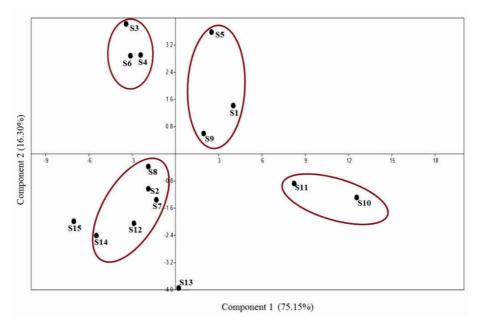


Figure 4. PCA for clustering of sites based on rate of contamination.

between the major contaminated sites and concentration of contaminants signifies the level of pollution in Guwahati city.

Thus the present study assesses the levels of pollutants in the industrial areas and areas of high traffic activity in Guwahati city. Total PAHs and heavy metals concentration in the samples close to the industrial areas and some high traffic areas were found to be significantly high. Differences in PAHs and metal contamination between the polluted and non-polluted areas also explain the intensity of soil pollution. Information obtained from PCA and correlations infers that vehicular emission and industrial effluents are major causes of contamination. Thus, proper soil quality monitoring is a prerequisite to curb these pollutants and prevent health hazards in the areas.

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## Measurement of tsunami wave eigenfunctions in deep, intermediate and shallower regions

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The present communication describes a numerical study and investigation of the excitation of tsunami waves by an earthquake. Detailed analysis has been carried out to describe the properties of eigenfunctions which represent the values of wave potential, horizontal and vertical velocity, and acceleration components with angular frequencies corresponding

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to the deep, intermediate and shallow water waves. Analysis and measurement of eigenfunctions were also performed. It shows that as distance progresses from the deep to coastal regions, celerity reduces due to increment in significant wave heights. At 80 km distance from the origin of generation, celerity is 550 m/s in deep, 440 m/s in intermediate and 310 m/s in shallow water waves.

**Keywords:** Earthquake, eigenfunctions, simulation. tsunami.

TSUNAMI is a system of ocean gravity waves formed as a result of large-scale disturbance of the seabed<sup>1</sup>. It is a type of ocean waves normally seen on the beaches<sup>2</sup>. Tsunamis may be characterized in terms of their mode of generation, propagation, wavelength, time period, velocity and distribution from the distinct oceanic regions to the coastal areas for a particular region of interest. With the comparative studies, it has been studied that the wind generated waves show lesser impact on the coastline as compared to tsunami generated waves because of different wave characteristics such as wavelength and velocity of propagation<sup>3,4</sup>. Deep and mid-sea movements, which are free of coastal contamination, are vital for realistic tsunami forecasting and source identification with increased experience in tsunami analysis and simulated measurements<sup>5</sup>. The initial displacements of the free surface of different water wave conditions are induced by larger earthquakes of magnitude of more than 9.0 on the Richter scale, in which the generation of N-type waves is higher<sup>6</sup>. The dispersion relationship shows the better response of wavenumber variations with respect to bathymetery depths for each water wave conditions. It carries the significance role while the calculation of all properties<sup>7</sup>.

Eigenfunctions are parameters involved in the study of distribution of wave motions with respect to variation of depth at a particular angular frequency of operation. The values of orbital velocity and distribution vary from deep to coastal waters<sup>8</sup>. Classification of deep and coastal water waves is made using correlations between depth and wavelength. If d/L < 1/20, it is known as shallow water condition, where d and L represent depth of ocean and wavelength respectively. If the ratio varies from 1/20 to 1/2, it is intermediate water condition<sup>9</sup>. If the ratio is more than 1/2, the region is considered as deep water. The impact at the coastal region is extremely high because a significant wave height increases due to less bathymetry as compared to the deep water<sup>10</sup>. Tsunami waves are known to shallow water waves. Airy wave theory is a linear theory for the propagation of waves on the surface of a potential flow and above a horizontal bottom. The free surface elevation  $\eta(x, t)$  of one wave component is sinusoidal, as a function of horizontal position x and time t (refs 11–13), the eigenfunctions can be derived using the following relationships.