Trace elements in the rainwater runoff of the urban catchment of Guwahati, India

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Abstract.   Rainwater runoff has been identified as a significant source of contaminants having tremendous impact on the receiving aquatic environment. In the present study, trace element transport by the surface runoff in the predominantly urban catchment of Guwahati city, India was monitored with a view to determine the chemical denudation rates of the land surface. A number of trace metals, namely Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were measured in the runoff after 70 major rain events within the city. Cadmium was found to be the least abundant metal and Iron was the most abundant metal in the runoff. The results are interpreted on the basis of temporal and spatial variations in their concentrations. These variations are quite large in some of the events and reflect changes in the local environmental setting, differences in water utilization, variations in runoff volume, gradient and quality.

1. Introduction

Surface runoff accounts for quite a considerable contribution to the total runoff from land, and carries with it various contaminants from the road surfaces, built-up areas and other settlements. Road surfaces accumulate significant quantities of pollutants including nutrients, metals and hydrocarbons originating from traffic activities (Tsihrintzis and Hamid 1997; Farm 2002). The runoff is considered a major source of the pollution in the environment (Lee *et al*. 2004).

Rapid urbanization is a global phenomenon, which attracts the researcher throughout the world in terms of its impacts on the environment. The consequent changes of urban traffic characteristics, such as increased volume and congestion, affect pollutant build-up on road surfaces (Zhao *et al*. 2010). The runoff quality is also important in identifying the nature of biogeochemical weathering processes (Tranter *et al*. 2002, Skidmore *et al*. 2004) and in characterizing the evolution of the drainage system (Sharp *et al*. 1995). The runoff is often the single most important factor in determining the sources of nutrients or toxic metals in the receiving waters (Prendez and Carrasco 2003). Clay, silt, finely divided organic and inorganic matter remain suspended in the runoff along with soluble and colored organic compounds, and plankton and other microscopic organisms giving the runoff a turbid look and contributing to the turbidity of the surface water sources and even shallow aquifers receiving the runoff.

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Road runoff is a major source of environmental pollution, significantly threatening nearby aquatic habitats. Chemical analyses have shown that the road "first flush" runoff is highly polluted (Dorchin and Shanas 2010) and there are considerable cumulative effects of the numerous pollutants in the runoff. Seasonal first flushes have high metal concentrations, and are likely to adversely affect the life in the receiving water bodies. In another recent work, Davis and Birch (2010) have measured trace metal transport by stormwater runoff from a major road and local street in urban Sydney, Australia from intensive sampling data. These authors have shown that copper, lead and zinc in the runoff had a logarithmic relationship to the total discharge from the roads in an event.

The interactions between runoff and catchment are dependent on chemical substances associated with the particulates and these may include sorption-desorption reactions, precipitation of Fe, Al, and Mn (oxi) hydroxides and co-precipitation of other metals (Mitchell *et al*. 2001, Poulton and Raiswell 2005). Major and minor elements transported by the runoff are predominantly found in the particulate-associated phase. The dynamic nature of the hydrological system and the associated changes in water discharge, suspended sediment load and water-sediment interactions control the seasonal variations in the concentration and flux of major, minor and trace elements in the dissolved state (Brown *et al*. 1996). The annual discharge volume of the runoff mostly covers the rainy season consisting of a period of 4-5 months of the summer.

In a recent assessment of water quality of first-flush roof runoff, Gikas and Tsihrintzis (2012) have observed that the runoff quality was satisfactory with respect to physicochemical parameters, but the sanitary quality was not good.

A new development has been the use of green (vegetated) roofs to improve the quality of runoff, although the impact is still not certain. A recent study has shown green roofs act as a source or a sink of various metals (Na, K, Ca, Mg, Al, Fe, Cu, Cd, Pb, Zn, Mn, Cr, Ni, Li and Co), inorganic anions and cations, their concentration strongly depending on the nature of substrates in the green roof and the volume of rain (Vijayaraghavan *et al*. 2012).

In the present work, fluctuations in contaminant transport by the runoff were studied over major rainfall events in the urban catchment area of the city of Guwahati, Assam (India).

2. Material and methods

2.1 Study area

Guwahati is a major city, the 'Gateway of the entire northeastern India', which has undergone rapid expansion in recent times with a consequent increase in population (Fig. 1). As per the 2011 census, population of Guwahati is 963,429. It is estimated that the population of the metropolitan area of Guwahati may vary from a low of 1.910 million to a high of 2.250 million in 2025. Guwahati is located approximately along $26°10^{'}$N latitude and $92°49^{'}$E longitude (GMDA 2007). The city is situated on undulating plain with varying altitudes of 49.5 m to 55.5 m above mean sea level (MSL). The central part of the city is interspersed with small hillocks like Sarania Hill (193 m), Nabagraha Hill (217 m), Nilachal hill (193 m), and Chunsali Hill (293 m). Structurally, this region is situated on the 50 m thick alluvium of the middle Brahmaputra valley.

Situated on the southern bank of the river Brahmaputra, Guwahati's projected population now
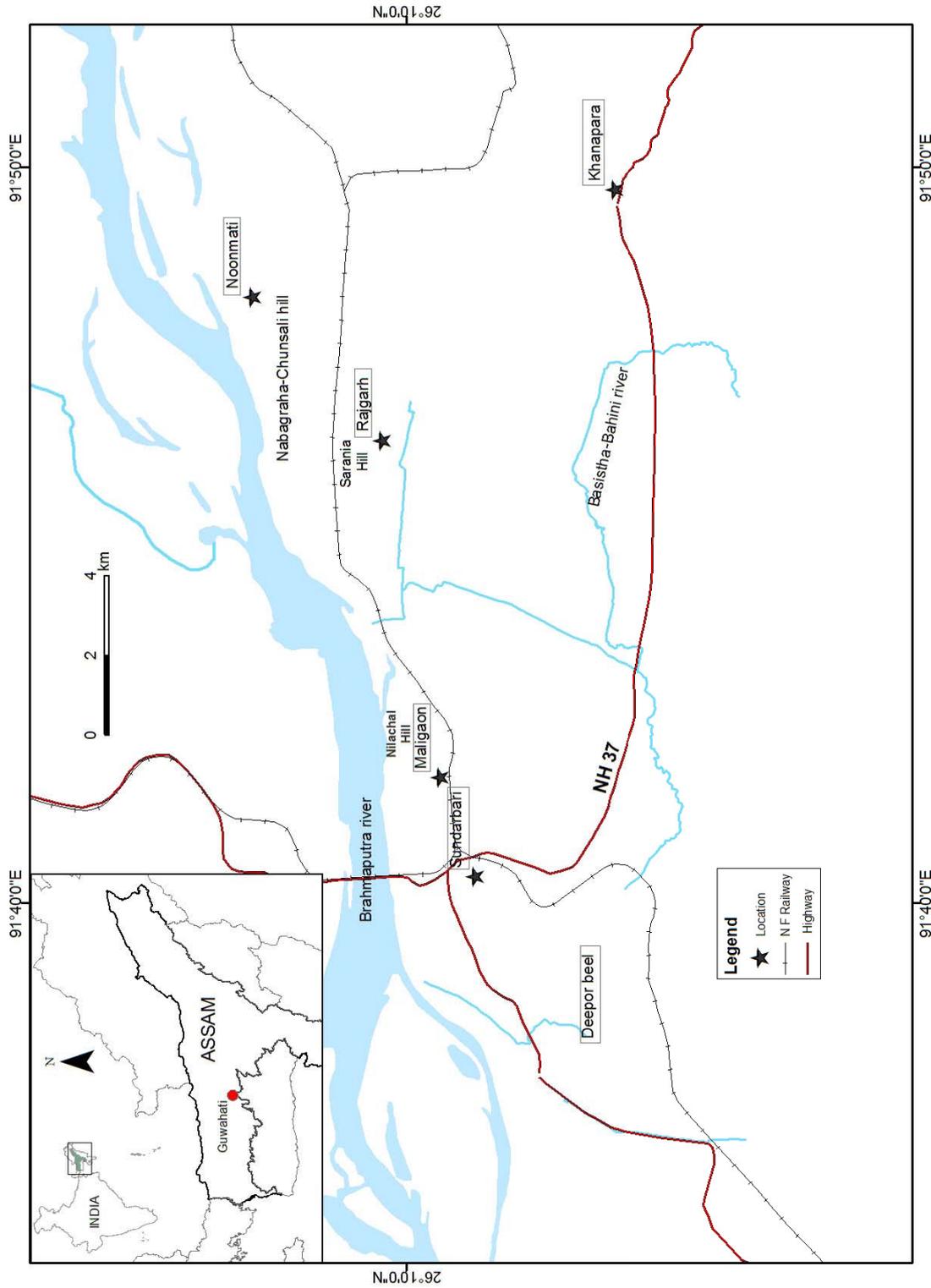
Fig. 1 The study area of Guwahati showing the sampling locations of Sundarbari, Noonmati, Khanapara, Maligaon and Rajgarh

is more than 1 million (GMDA 2007). Guwahati's 'urban form' is somewhat like a starfish. With a core in the central areas, the city has tentacles extending in the form of growth corridors towards south, east and west.

The city is the main corridor for passage to the states of Assam, Meghalaya, Mizoram, Tripura, Manipur, Nagaland and Arunachal Pradesh and all the roads, including the two highways, NH31 and NH37, passing through the city, are busy with vehicular traffic day and night. The establishment of the Guwahati refinery (Indian Oil Corporation Limited, capacity 1 million ton) at Noonmati and other industries also contribute to rapid development of the city. Being the nerve-centre of the political, social, and cultural activities of the entire northeastern India in general and of the state of Assam in particular, Guwahati has become practically the capital of the entire region.

The climate is homogenous over the city. The principal characteristics are a cold and foggy winter (December-February), a moderately cool spring (March-May), a fairly hot and humid summer (June-August) and a pleasant autumn (September-November). However, there are no rigid boundaries between the seasons. Summer temperatures range from a minimum of 22 degrees to a maximum of 38 degrees Celsius. Winter temperatures range from a minimum of 10 degrees to a maximum of 25 degrees Celsius. The average annual rainfall is 180 cm during the months of May to September.

2.2 Surface runoff sampling

The surface runoff was collected at five selected locations along the major road systems in the city during and immediately after major rain events of April to October at 10–30 minutes intervals. Plastic containers of 1 L capacity, detergent cleaned, acid rinsed, washed with de-ionized water several times, and dried, were used for sampling. The runoff samples were immediately filtered through Whatmann 42 filter paper, stored and analyzed as per standard procedure (APHA 1995).

The details of sampling locations and frequency are given in Table 1.

The location, Sundarbari (S) is located in the western part of the city of Guwahati. It can be considered as the traffic junction for vehicles coming to and going from Guwahati to northern, eastern and western parts of the state including interstate traffic. This location also holds the campus of Gauhati University with other residential areas and vegetable markets. A considerable amount of construction activities, including making a bypass of the National Highway NH37 are going on. Seven different runoff events, stretching from 10 to 60 minutes, were covered in this location.

The location, Noonmati (N) has grown around the Indian Oil Refinery and is both industrial and residential in nature. It is also a traffic hub connecting the city to the eastern parts of greater Guwahati as well as the district of Morigaon. The area has low and medium hills all around and is also close to Railway Good Yard at New Guwahati. The runoff at this location was collected as it comes down a slope from 3 different events with rain occurring from 30 to 100 min.

Three major rain events were covered in runoff sampling from the location, Khanapara (K). This is one of the main traffic junctions of the city, receiving thoroughfare from upper Assam as well as the state of Meghalaya moving through the city to different destinations. The area is also known for the location of the Veterinary College campus of the Assam Agriculture University, Government offices, business establishments and resorts. The rain events at this location were of duration 10 to 60 min.

The fourth location, Maligaon, (M) is a hub of business and traffic, and all thoroughfares to the

west of the city as well as to the north bank of the River Brahmaputra, cross through this location. Maligaon is also the Head Quarter of the Northeast Frontier Railway and has expanded tremendously in recent times with business and commerce. Three different rain events lasting from 45 to 100 min were covered in this location and the runoff samples were collected from the roadside.

The location, Rajgarh (R), is mainly a residential area with a considerable amount of traffic. As this location is almost at the centre of the city, a large number of vehicles crisscross across in various directions of the city. Runoff samples were collected after three different events of duration 10 to 60 min.

2.3 Physico-chemical analysis

The pH of each sample was read immediately after collection with a digital pH-meter (Elico pH-Meter Model LI 127) using standard buffers of pH 4 and 9 for calibration purposes.

The runoff samples immediately after collection were acidified to pH < 2.0 by adding concentrated HNO_3 drop-wise. After acidification, the samples were stored in a refrigerator at ~ 4°C till analysis for the metals was undertaken. Since the water samples were mostly turbid with appreciable load of suspended particulates, the water samples were digested to find the

Table 1 Details of locations and sampling frequency of the runoff

S/N	Site location		Site name	Rain event	Runoff samples at intervals of 5 min					
	Latitude (N)	Longitude (E)								
1	26°09'05.0"	091°40'21.4"	Sundarbari	I	S1	S2				
				II	S3	S4				
				III	S5	S6				
				IV	S7	S8	S9	S10		
				V	S11	S12				
				VI	S13	S14	S15	S16		
				VII	S17	S18	S19	S20		
2	26°12'04.3"	091°48'14.2"	Noonmati	I	N1	N2				
				II	N3	N4	N5	N6		
				III	N7	N8	N9	N10	N11	N12
3	26°07'13.2"	091°49'41.6"	Khanapara	I	K1	K2				
				II	K3	K4	K5	K6		
				III	K7	K8	K9	K10	K11	K12
4	26°09'33.1"	091°41'42.2"	Maligaon	I	M1	M2	M3			
				II	M4	M5	M6			
				III	M7	M8	M9	M10	M11	M12
5	26°10'19.8"	091°46'16.9"	Rajgarh	I	R1	R2	R3	R4	R5	R6
				II	R7	R8				
				III	R9	R10	R11	R12	R13	R14

concentration of both dissolved metals and that associated with the particles. In this work, nitric acid digestion technique (APHA 1995) was used.

The trace metals, namely, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analyzed by Atomic Absorption Spectrometer (PerkinElmer Analyst 200) using three standards calibration curve.

3. Results and discussion

The experimental data are presented in Table 2(a)-(e) for the five locations.

3.1 pH

The pH of the runoff spread from 4.6 to 7.8, but, in most cases, the runoff had pH near 7.0, and therefore, the runoff can neither be categorized as acidic nor alkaline.

The variations in pH were different for each of the five locations. This is indicated by the way the maximum, the mean and the median values of pH for each location varied (Fig. 2). The values had different diurnal trends from one event to another. Thus, for the location S, the pH decreased diurnally in five of the seven events, but in the remaining two events, there was an increasing trend. Such unpredictable behaviour was seen in the other locations as well. Only in case of location M, the pH decreased with time in all the three events measured. One interesting result was for the location R, where the pH showed a continuous increase with time in the third event. The extremes of pH are large in the locations, S and N. The decrease in pH of the runoff with time might be due to leaching of acidic elements such as Al and Fe from the soil that replaced Ca and Mg in the runoff.

The pH of natural rainwater is often taken to be 5.6, which is due to the global atmospheric concentration of CO_2 (330 ppm). However, CO_2 is not the only background trace constituent that is capable of influencing the pH of rainwater. The processes controlling the composition of rain are
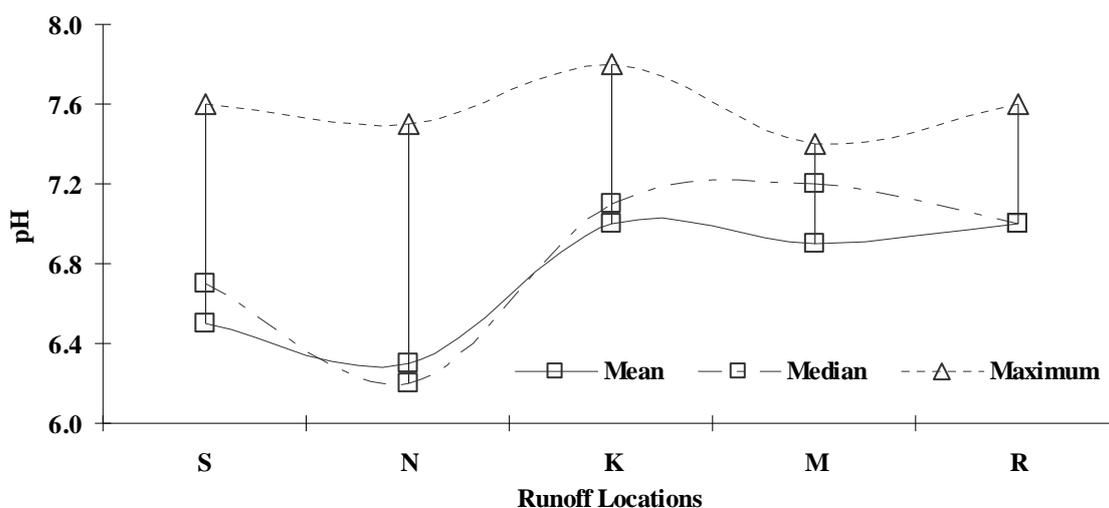

Fig. 2 Variation of pH of the runoff at the five locations

Table 2(a) Experimental data for location S

Sample	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S1	7.1	0.018	0.068	2.947	BDL	1.190	1.022	0.004	BDL	0.067
S2	6.9	0.012	0.064	2.33	BDL	0.792	0.631	0.002	BDL	0.048
S3	5.1	0.014	0.032	1.233	BDL	0.441	0.660	BDL	BDL	0.066
S4	5.7	0.012	0.051	0.752	BDL	0.152	0.669	0.001	BDL	0.068
S5	7.1	0.013	0.068	0.825	BDL	0.187	0.480	BDL	BDL	0.078
S6	6.0	0.007	0.056	0.765	BDL	2.268	0.469	0.003	BDL	0.194
S7	7.6	0.011	0.079	BDL	BDL	0.406	0.491	0.004	BDL	0.396
S8	6.9	0.013	0.069	BDL	BDL	0.160	0.480	0.007	BDL	0.169
S9	6.8	0.009	0.064	BDL	BDL	0.336	0.451	0.003	BDL	0.178
S10	6.6	0.006	0.062	BDL	0.051	0.145	0.411	0.003	BDL	0.230
S11	7.1	0.012	0.558	BDL	0.446	1.608	0.144	0.019	0.283	0.044
S12	7.6	0.010	0.704	BDL	0.234	0.488	0.243	0.022	0.200	0.039
S13	7.1	BDL	0.895	0.006	0.202	0.160	BDL	0.069	0.195	0.067
S14	6.7	BDL	0.538	0.003	0.225	0.370	BDL	0.043	0.109	0.075
S15	6.7	BDL	0.627	0.010	0.232	0.410	BDL	0.046	0.211	0.070
S16	6.6	BDL	0.690	0.009	0.255	0.415	BDL	0.500	0.188	0.055
S17	6.1	BDL	0.762	0.044	0.148	1.661	BDL	0.071	0.012	0.109
S18	6.3	BDL	0.729	0.021	0.105	4.937	BDL	0.059	BDL	0.115
S19	4.6	BDL	0.773	0.079	0.288	1.521	BDL	0.178	BDL	0.166
S20	5.0	BDL	0.811	0.017	0.354	1.786	BDL	0.173	0.019	0.172
Min	4.6	0	0.032	0	0	0.145	0	0	0	0.039
Max	7.6	0.018	0.895	2.947	0.446	4.937	1.022	0.5	0.283	0.396
Mean	6.48	0.007	0.385	0.452	0.127	0.972	0.308	0.060	0.061	0.120
Std Dev	0.836	0.006	0.341	0.839	0.142	1.144	0.308	0.116	0.096	0.087

complex and influenced by both natural and anthropogenic sources. Rainwater pH values, in the absence of common basic compounds such as NH_3 and $CaCO_3$ may be expected to range from 4.5 to 5.6 due to natural sulfur compounds alone (Charlson and Rodhe 1982, Melidis *et al.* 2007). Various sorption/desorption reactions as well as chemical complexation with inorganic and organic ligands, redox reactions controls the leaching and bioavailability of metals which can affect the pH of runoff water (Violante *et al.* 2010).

3.2 Trace metals

Significant levels of metals are found in urban and in highway runoffs from many investigations. Among a variety of metals present in storm water, cadmium, copper and lead are the most hazardous ones. Concentrations of copper, lead, and cadmium appear to be directly correlated to traffic intensity on surfaces such as highways, streets, and parking lots (Davis and Shokouhian 2001).

Table 2(b) Experimental data for location N

Sample	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
N1	7.5	0.003	0.047	BDL	0.061	0.495	0.375	0.007	BDL	0.142
N2	7.4	0.013	0.049	BDL	0.022	1.633	0.449	0.005	BDL	0.291
N3	6.6	0.008	0.052	BDL	0.095	1.476	0.456	0.020	BDL	0.325
N4	6.5	0.006	0.048	BDL	0.039	0.528	0.391	0.006	BDL	0.270
N5	6.4	0.024	0.027	BDL	0.044	0.358	0.416	0.002	BDL	0.272
N6	6.4	0.013	0.020	BDL	0.028	0.798	0.540	0.005	BDL	0.303
N7	5.9	BDL	0.630	BDL	0.220	4.740	0.064	0.158	0.080	0.050
N8	5.4	BDL	0.345	BDL	0.334	6.746	BDL	0.134	0.029	0.066
N9	5.6	BDL	0.650	BDL	0.614	12.297	0.005	0.185	0.018	0.043
N10	5.7	BDL	0.670	BDL	0.338	10.264	BDL	0.079	0.012	0.064
N11	5.7	BDL	0.522	BDL	0.200	6.746	BDL	0.081	0.017	0.064
N12	6.0	BDL	0.543	BDL	0.286	6.028	0.087	0.031	0.014	0.072
Min	5.4	0	0.020	0	0.022	0.358	0	0.002	0	0.043
Max	7.5	0.024	0.670	0	0.614	12.297	0.54	0.185	0.080	0.325
Mean	6.3	0.006	0.300	0	0.190	4.342	0.232	0.059	0.014	0.164
Std Dev	0.7	0.008	0.283	0	0.180	4.115	0.220	0.067	0.023	0.117

Table 2(c) Experimental data for location N

Sample	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
K1	6.9	0.014	0.029	0.181	BDL	0.527	0.550	0.006	BDL	0.078
K2	6.5	0.009	0.036	1.446	BDL	0.456	0.765	0.007	BDL	0.024
K3	6.3	0.010	0.050	0.541	BDL	0.483	0.597	0.004	BDL	0.125
K4	6.6	0.005	0.053	0.561	BDL	0.102	0.580	0.006	BDL	0.080
K5	6.6	0.016	0.058	1.433	BDL	0.155	0.570	0.009	BDL	0.064
K6	5.7	0.021	0.035	0.781	BDL	0.127	0.393	0.005	BDL	0.038
K7	7.8	0.009	0.643	0.177	0.242	1.210	0.342	0.080	0.387	0.099
K8	7.4	BDL	0.560	0.006	0.154	1.410	0.091	0.027	0.332	0.041
K9	7.5	BDL	0.433	BDL	0.183	0.643	0.089	0.069	0.119	0.102
K10	7.4	BDL	0.495	BDL	0.177	0.716	0.123	0.070	0.369	0.049
K11	7.4	0.011	0.456	BDL	0.258	1.099	0.095	0.042	0.253	0.088
K12	7.3	0.007	0.555	BDL	0.114	5.322	0.115	0.004	0.395	0.113
Min	5.7	0	0.029	0	0	0.102	0.089	0.004	0	0.024
Max	7.8	0.021	0.643	1.446	0.258	5.322	0.765	0.08	0.395	0.125
Mean	7.0	0.009	0.284	0.427	0.094	1.021	0.359	0.027	0.155	0.075
Std Dev	0.6	0.007	0.256	0.542	0.105	1.420	0.249	0.030	0.177	0.032

Table 2(d) Experimental data for location M

Sample	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
M1	7.3	0.010	0.078	1.289	BDL	0.151	0.573	0.008	BDL	0.063
M2	6.9	0.014	0.061	1.736	BDL	0.189	0.524	0.006	BDL	0.066
M3	6.5	0.008	0.046	1.606	BDL	0.570	0.558	0.004	BDL	0.096
M4	7.4	0.011	0.091	0.582	BDL	0.270	0.569	0.009	BDL	0.088
M5	6.0	0.015	0.033	0.308	BDL	0.363	0.548	0.008	BDL	0.118
M6	5.6	0.012	0.073	0.097	BDL	0.266	0.599	0.005	BDL	0.064
M7	7.3	BDL	0.529	0.055	0.271	0.688	BDL	0.018	0.027	0.079
M8	7.3	BDL	0.693	0.120	0.283	0.636	BDL	0.055	0.059	0.067
M9	7.2	BDL	0.659	0.109	0.265	0.423	BDL	0.043	0.006	0.171
M10	7.2	BDL	0.681	0.039	0.247	0.328	BDL	0.086	0.079	0.096
M11	7.1	BDL	0.382	0.004	0.121	0.135	BDL	0.006	0.032	0.081
M12	6.9	BDL	0.387	0.110	0.267	0.485	BDL	0.107	0.051	0.117
Min	5.6	0	0.033	0.004	0	0.135	BDL	0.004	0	0.063
Max	7.4	0.015	0.693	1.736	0.283	0.688	0.599	0.107	0.079	0.171
Mean	6.9	0.006	0.309	0.505	0.121	0.375	0.281	0.030	0.021	0.092
Std Dev	0.6	0.006	0.275	0.653	0.133	0.187	0.294	0.036	0.028	0.031

Table 2(e) Experimental data for location R

| Sample	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
R1	7.5	0.019	0.079	BDL	BDL	0.246	0.642	0.010	BDL	0.188
R2	7.3	0.021	0.054	BDL	BDL	0.498	0.495	0.007	BDL	0.287
R3	7.6	0.012	0.086	BDL	BDL	0.778	0.581	0.006	BDL	0.216
R4	7.2	0.014	0.056	BDL	BDL	0.105	0.583	0.011	BDL	0.052
R5	7.2	0.018	0.103	0.044	BDL	0.273	0.481	0.007	BDL	0.119
R6	6.4	0.016	0.091	BDL	BDL	0.406	0.491	0.004	BDL	0.169
R7	7.2	0.012	0.073	0.097	BDL	0.266	0.599	0.007	BDL	0.221
R8	7.1	0.016	0.084	BDL	BDL	0.318	0.569	0.008	BDL	0.200
R9	6.5	BDL	0.235	BDL	BDL	4.606	BDL	0.132	BDL	0.302
R10	6.6	BDL	0.462	BDL	0.019	8.144	BDL	0.105	0.011	0.229
R11	6.7	BDL	0.797	BDL	0.011	9.974	BDL	0.170	0.009	0.219
R12	6.7	BDL	0.583	BDL	BDL	9.724	BDL	0.150	0.005	0.208
R13	6.8	BDL	0.577	BDL	BDL	7.964	BDL	0.165	0.032	0.201
R14	6.9	BDL	0.341	BDL	BDL	7.043	BDL	0.135	0.015	0.225
Min	6.4	BDL	0.054	0	0	0.105	0	0.004	0	0.052
Max	7.6	0.021	0.797	0.097	0.019	9.974	0.642	0.17	0.032	0.302
Mean	7.0	0.009	0.259	0.010	0.002	3.596	0.317	0.066	0.005	0.203
Std Dev	0.4	0.009	0.249	0.028	0.006	4.066	0.288	0.071	0.009	0.062
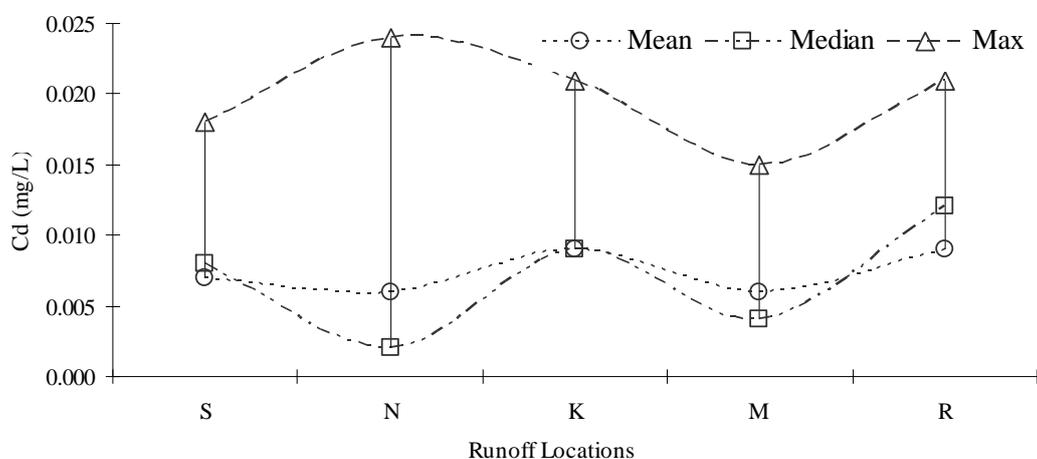
Fig. 3 Concentration variation of Cd in the runoff

Cadmium (Cd), a naturally occurring element, is a potentially biotoxic metal in terrestrial and aquatic ecosystems. In the runoff, it could be found from below detection level (BDL) to 0.024 mg/L. In total, 29 of the samples (41%) had values below detection level and the sample N5 had the maximum value.

Cadmium was one of the least abundant metals found in the surface runoff. The site-wise variation in the maximum, the mean and the median values of Cd for the different events taken together (Fig. 3) shows that while the median value is very close to the mean value at all the locations, the maximum differs from these very much, particularly at the location N. Thus, in some events, Cd can have extremely large value at this location. The values had different diurnal trends from one event to another. In case of the location S, the values showed decreasing diurnal trend for five events namely I, II, III, IV and V while no Cd could be detected in two of the events, VI and VII. For location N, event I had an increasing trend and event II both decreasing and increasing trends. For the location M, an increasing trend was followed by a decreasing one for two of the events, I and II. In case of K and R events, there was no specific variation trend.

Cadmium may have entered the runoff via leaching of soil which occurs through soil-plant systems, while plant Cd uptake varies with crop type (Longhurst *et al.* 2004). It is common for the particulate associated and dissolved Cd loss via surface runoff as Cd sorbs to and accumulates in the top soils; hence erosion becomes significant form of Cd loss (Edwards and Withers 2008). Cadmium may enter water from industrial processes such as the smelting and refining of ore minerals, electroplating and paint manufacturing, combustion of fossil fuels, and also from the application of phosphate fertilizers (Mermut *et al.* 1996), leaching from contaminated landfill or from soil having sewage sludge dumping. The concentration in unpolluted water is < 1 μg/L. A set of experiments (McDowell 2010) using simulated rainfall to generate surface runoff indicated that the major form of Cd lost was dissolved (on average 65%, < 0.45 μm) and could be predicted by water extraction of the soil.

Cobalt in the runoff was distributed from 0.020 mg/L (N6) to 0.895 mg/L (S13) (Fig. 4). The location S had decreasing trends in I, III and IV events, increasing trend in II and V events and the other two events had decreasing as well as increasing trends. For location N, increasing trend was found for event I, decreasing trend for event II and no specific diurnal trend for event III. For
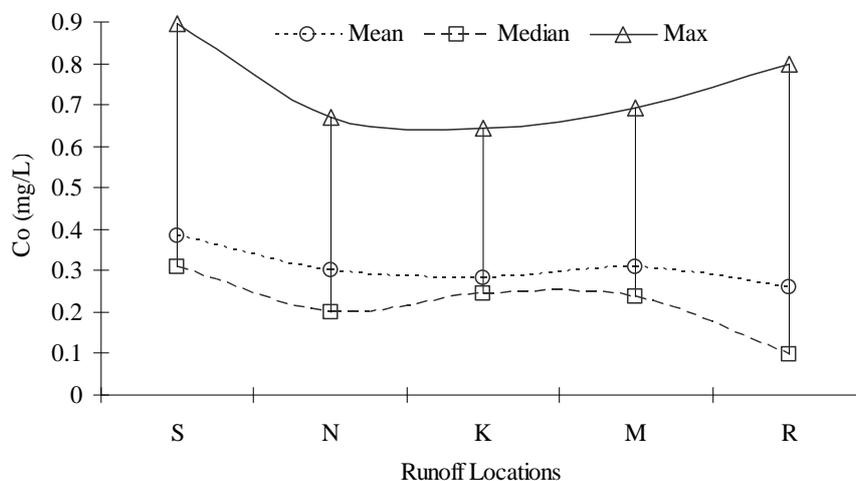
Fig. 4 Variation of the concentration of Cobalt in the runoff

location K, Co increased diurnally for event I, while the event II had both increasing and decreasing trends and no specific trend for the event III. In location M, event I had a decreasing trend while no specific diurnal trend could be observed for the events II and III. In location R decreasing trend was found for the event II and the events I and III had no specific trend. The cobalt concentration is found to be inversely correlated to the pH values for the locations S, N and R. Moore (1991) has shown that the concentration of cobalt in aquatic environments relate significantly to pH in an inverse correlation and to suspended solids in a positive correlation.

Cobalt, an essential element for growth, is a constituent of Vitamin B_{12}. However, in higher concentrations cobalt is toxic to humans and to terrestrial and aquatic animals and plants. Acute exposure to cobalt may lead to a depression in iodine uptake, anorexia, nausea, vomiting and diarrhoea (Nagpal 2004).

In the present work, the runoff from different rain events had total Cr content from BDL to 2.947 mg/L. The variations of the mean, median and maximum Cr contents (Fig. 5) show a few significant features: Cr was very low or negligible at the locations, N and R, but the other three locations had extreme values that differed largely from the mean or the median values. This was particularly so at the location S. It is to be noted that Cr could not be detected in 22 of the runoff samples (31%). The highest Cr content of 2.947 mg/L was measured for the sample S1. For this location S, the events I, II and III had Cr decreasing with time while the events, IV and V, had values below detection level and the events, VI and VII, had both decreasing and increasing trends. All the samples at the location N had values below detection level. For the location M, the event I showed increasing followed by decreasing trends, the event II decreasing trend and the event III no particular trend. The other locations K and R did not show any specific trend.

Chromium occurs in the Earth's crust with the main natural source of exposure being continental dust present in the environment (Pellerin and Booker 2000). Chromium is exposed to the water by industrial releases and it accounts for the majority of the anthropogenic releases.

The electroplating, leather tanning, and textile industries release large amounts of chromium to surface waters (Johnson et al. 2006). It is also released into the environment in larger amounts as a result of human activities, which account for 60–70% of the total emissions of atmospheric
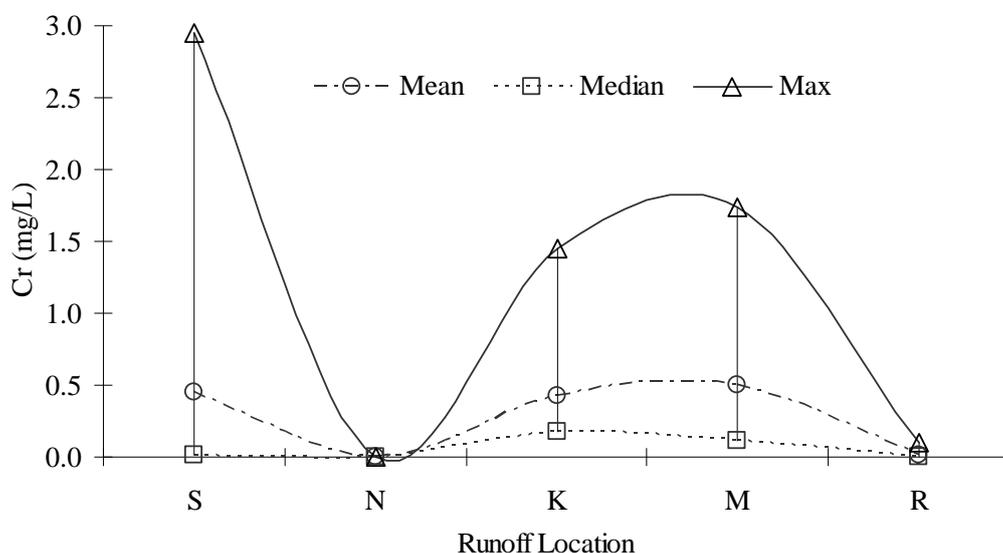
Fig. 5 Variation in the concentrations of Chromium in the runoff

chromium. Facchinelli (2001) have found the distribution of Cr in a predominantly agricultural area in Italy to be influenced by natural sources. The mean concentration of chromium in rainwater is 0.14–0.9 μg/L (Dasch and Wolff 1989). Chromium exists in the oxidation states of +3 and +6 and the latter is the stable as well as the more toxic form. Cr (VI) is also the more mobile form in the soil environment than the trivalent form (Ramesh and Anbu 1996). At lower soil pH values, the mobility of Chromium (III) in soil may increase due to the formation of soluble complexes with organic matter in soil, potentially facilitating contamination to the runoff (Avudainayagam *et al*. 2003).

Copper concentration in the rainwater runoff was from below detection level (BDL) to 0.614 mg/L at Guwahati. Fig. 6 shows that extreme values of Cu were recorded at the locations, S and N. The sample N9 had the maximum Cu content. 33 of the samples (47%) had Cu below detection level. At the location S, Cu could not be detected in the events, I, II, III, and three samples of the event IV. Event V had decreasing trend while event VI had increasing trend and for the event VII, Cu content decreased first and then increased. For location N, the events I and II, showed decreasing trend while the event III showed increasing, decreasing, and increasing trends. For location M, Cu content was below detection level for the events, I and II, and there was no uniform trend for the event III. For location K and R, there was no specific trend. For location N, there was a decreasing trend for the first two events and while no trend could be seen for the last event.

Copper is consistently added to soils in the form of fertilizers, pesticides, livestock manures, sewage sludge, and industrial emissions (Adriano 1989). This metal has moderate mobility under slightly acid soil conditions (Hesterberg *et al*. 1993). There is thus a potential for entry of Cu from nonpoint-sources and the possibility of Cu transport from soil to water. Copper accumulate in soils in water-soluble, exchangeable, carbonate-associated, oxide-associated, organic-associated, and residual forms. Water-soluble and exchangeable fractions would be readily released to the runoff, whereas the residual fraction is immobile under natural conditions.
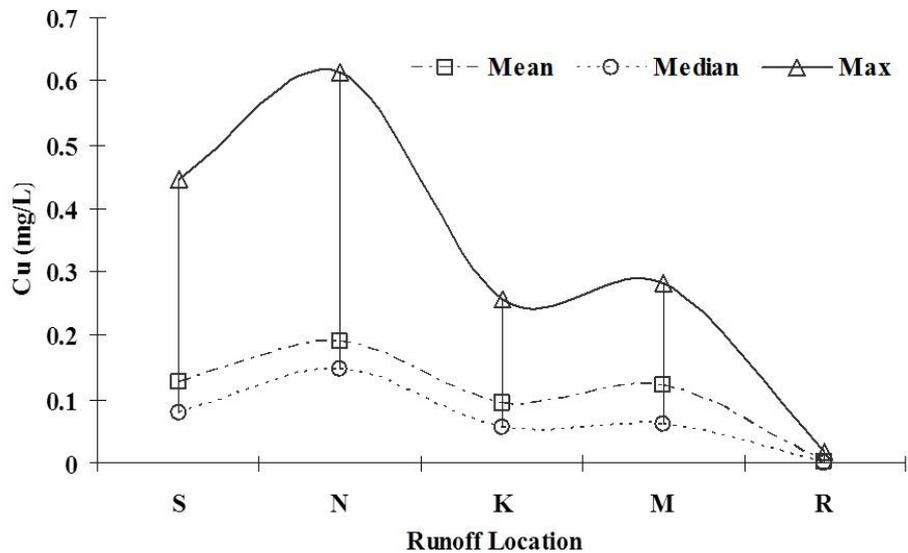
Fig. 6 Concentration of Copper in the runoff and its variation
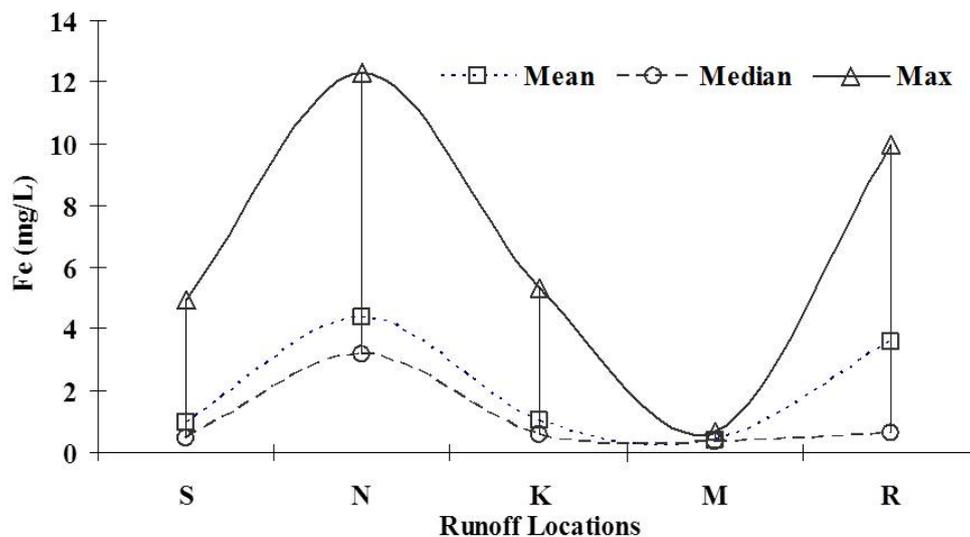

Fig. 7 Variation in the concentration of Iron in the runoff

Iron in the runoff varied from 0.102 to 12.297 mg/L with the location M showing minimum variations and the locations, N and R, having the widest range of values (Fig. 7). Iron is the most abundant metal in the surface runoff. In the location S, Iron showed decreasing trend for the events I, II and V; increasing trend for the events III and VI; and for the remaining events IV and VII showed no regular trend of Iron content.

For location N, the event I had an increasing trend, event II showed initially decreasing and then increasing trend, and event III showed initially increasing and afterward decreasing trend. For location K, decreasing trend was seen for the event I while the events II and III did not show any

regular trend. For location M, the event I showed increasing trend while the events II and III again had no significant trend. For location R, the event II showed increasing trend of Iron content in the runoff, but the events I and III had no distinct trend. The water solubility of some iron compounds increases at lower pH values. There is a negative correlation of iron with pH in the runoff. Usually there is a difference between water soluble Fe^{2+} compounds and water insoluble Fe^{3+} compounds. The latter are only water soluble in strongly acidic solutions, but water solubility increases when these are reduced to Fe^{2+} under certain conditions.

Iron is ubiquitous in all freshwater environments and often reaches significantly higher concentrations in water and sediments than other trace metals due to its highest abundance in earth crust (Forstner and Wittmann 1979).

Ferric hydroxide and Fe-humus precipitates on biological and other surfaces, affect lotic organisms by disturbing the normal metabolism and osmoregulation through change in the structure and quality of benthic metals and habitants and food resources. Iron contamination decreases the species diversity and the abundance of periphyton, benthic invertebrates and fish. Iron may be harmful to plants at feed concentrations of between 5 and 200 ppm. Sorption and co-precipitation of metals by Fe-oxidation decreases the bioavailability and toxicity of water-borne metals, but may increase the dietary supply of metals and lead to toxic effects along the food chain (Vuori 1995).

The runoff had Mn in the range of BDL to 1.022 mg/L. The sample S1 had the maximum Mn content. One significant feature of Mn contents is that in all the locations, the mean and the median values are similar excepting the location, R (Fig. 8). The extreme values differed by almost the same amount from the mean at the locations, N, K, M and R, but the difference is much more at the location, S. The rainwater runoff samples of the five locations had Mn below detection level in 23 of the samples (33%). For the location S, the values decreased for three events, I, III and IV; increased for two events II and V; and the remaining two events, VI and VII, had BDL values. For the location N, Mn showed increasing trend for the event I, and no specific trend for the events,
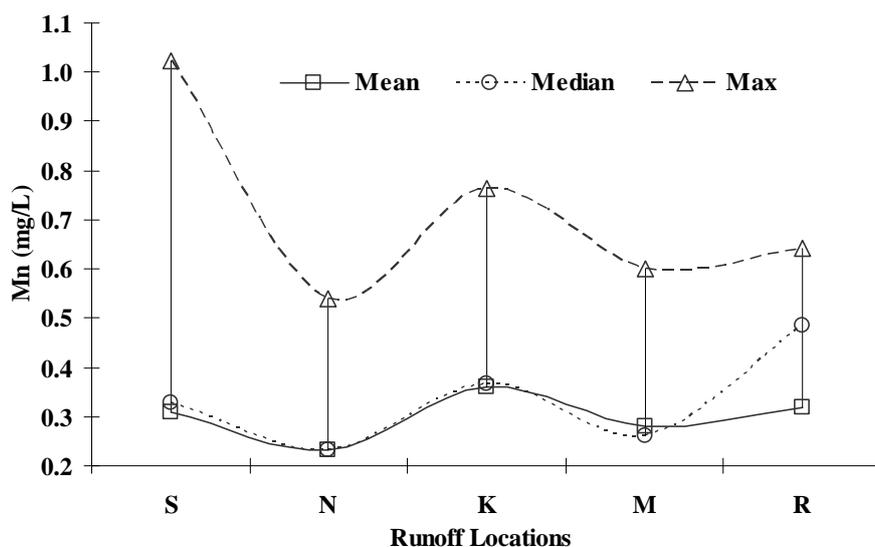

Fig. 8 Concentration of Mn in the runoff and its variations

II and III. For the location K, increasing trend was observed for the event I, decreasing trend for the event II and no specific trend for the event III. For the location M, the values first decreased and then increased for the two events, I and II, and no manganese was detected for the event, III. For the locations R, there was no specific trend.

Naturally, manganese oxides are found in various forms of discrete particles, coatings, nodules, micro-nodular deposits, thin layers on mineral surfaces, or interspersed in clay minerals (Koljonen *et al.* 1976). These oxides tend to be deposited at the redox front which may occur near the water table and also at places along the ground-water flow path owing to changes in vertical and horizontal permeability. Under favorable conditions of water circulation pattern and/or chemical composition, these salts can be redissolved (Lind *et al.* 1987) and leached into the runoff.

Nickel contents of the runoff were in the range of BDL to 0.5 mg/L with the maximum value at S16. Very large variance between the maximum Ni-content and either the mean or the median Ni-content was observed at the location, S (Fig. 9). Only two of the samples (2.9%) had BDL value for Ni. For the location S, no particular trends could be observed for the different events, but the events VI and VII recorded very high Ni contents. For the location N, decreasing trend was seen for the event I; no specific diurnal trend for the events II and III. The same was observed for the location K. For the location M, decreasing trend was seen for the events, I and II, and no specific trend for the event III. For location R, decreasing trend was seen for the event II and no specific trend for the events, I and III.

Most of the dissolved Ni in surface runoff is likely to occur in complexed form. Moderately strong metal-complexing ligands in the form of humic substances are responsible for the complexation of about 20% of Ni and the remaining Ni is complexed by ligands with apparent stability constants comparable to those of synthetic chelating agents (Sedlak *et al.* 1997).

Lead occurred in the runoff in contents of BDL to 0.395 mg/L, the highest value being measured for the sample K12. 38 of the samples (54%) recorded BDL values. For the location S,
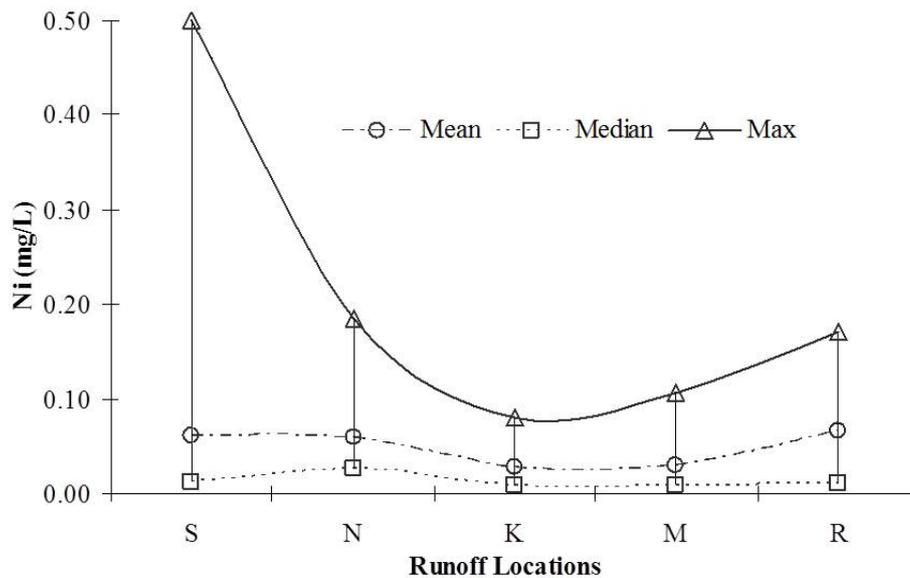

Fig. 9 Concentration variations for Nickel in the runoff

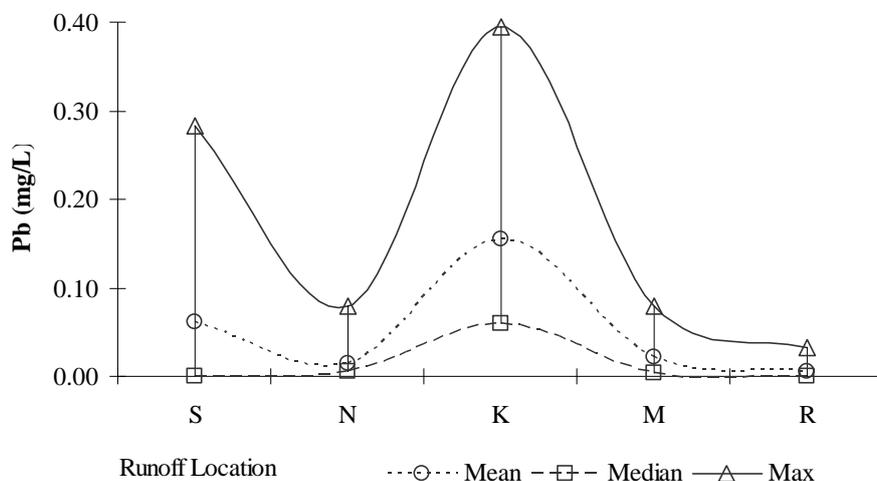*Upama Devi and Krishna G. Bhattacharyya*

Fig. 10 Variations in Pb concentrations in the runoff

Lead was not detected for the first four events I, II, III and IV; for the event V there was decreasing trend and for the events, VI and VII, no specific trend was observed. For the location K, R and M, there was no particular trend in Pb content in the runoff. For location N, the first two events I and II had Pb below detection level and the event III had a decreasing trend with time. Fig. 10 shows that the variations in the Pb-contents were maximum at the location K, followed by the location S. The variations were minimum at the other three locations.

The main source of lead in the atmosphere was the tetraethyl lead used in gasoline to improve the octane number. This has been discontinued but the deposition from earlier use might have remained in the urban soil. Also, many soils contain appreciable amount of Pb from natural sources. Being mostly insoluble, the runoff can remove only a small part of Pb in the roadside urban soil. In this context, Pb-content of the runoff at some of the locations can be described as
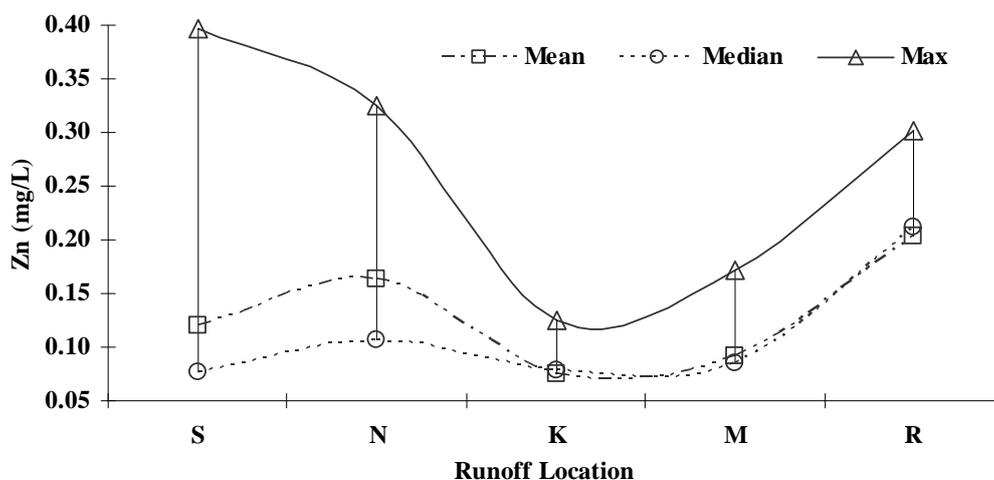

Fig. 11 Concentration of Zn in the runoff and its variation

sources. Being mostly insoluble, the runoff can remove only a small part of Pb in the roadside substantial. Lead is a cumulative poison, initiating hypertension, tiredness, irritability, anemia, behavioral changes, and impairment of intellectual functions in affected patients (Tebbutt 1983). Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can affect adversely to nervous system and kidneys (Mugica and Maubert 2002).

The runoff had Zinc from 0.024 to 0.396 mg/L. The sample K2 had the minimum value and S7 had the maximum value. For the location S, decreasing trend was seen for the three events I, V and VI, increasing trend for the three events II, III and VII and both type of trends for the event IV. For the location K, decreasing trend was seen for the two events I and II and no specific trend for the event III. For the location M, there was increasing trend found in the event I, and no specific trend for the events, II and III. In the location R, Zn showed an irregular trend for the event I, decreasing trend for the event II and decreasing-increasing trend for the event III. For location N, Zinc was found in increasing trend for the event I; no uniform trend for the events II and III. The plots of the mean, the median and the maximum Zn-contents (Fig. 11) show very similar variations at the locations, K, M and R, but the differences are very large at the locations, S and N.

According to Hewitt and Rashed (1990), zinc is produced mainly from vehicle tyre wear and the corrosion of galvanized steel crash barriers and brake linings. It is likely that the runoff had leached Zn from the soil receiving Zn from these sources.

It is likely that the metal contents of surface soil had some influence on the movement of metals, especially in sandy soils (Cezary and Singh 2001), and the concentrations of heavy metals in runoff are dependent on their presence in soil, particularly near the urban highways (Turer *et al.* 2001).

4. Discussion

The present work yielded data on the quality of the surface runoff at Guwahati city. The locations chosen for sampling in this work are major traffic junctions of the city and therefore, the runoff quality can be correlated with the deposition of contaminants on the road surface mainly from vehicular emissions and vehicle wear and tear. However, it is also observed that the runoff is not equally affected at all the five locations, showing different levels of anthropogenic activities. The distribution of the metals in the runoff does not follow uniform and identifiable trends. In particular, the following conclusions may be drawn:

(a) The observed pH of the runoff varied from 4.55 to 7.83 i.e., acidic to slightly basic. The results indicated that the pH was controlled by leaching of acidic elements such as Al and Fe from the soil that replaced Ca and Mg. The average pH of the runoff samples was 6.69, probably due to neutralization. Only four samples (5.7%) had the pH below 5.6. This may be an indication of alkaline contamination of the rainwater as the pH of natural water is ~ 5.6.

(b) Cadmium was found to be positively correlated with pH of the runoff for the sites, S, N and R which showed that this metal enters into the runoff from the surrounding topsoil at higher pH.

(c) In contrast, Cobalt was inversely correlated with pH at three of the five sites, namely, S, N and R. Thus, more and more Co leaches into the runoff from the topsoil as pH goes down.

(d) Cobalt is the most abundant metal and Cadmium was found to be the least abundant metal in the surface runoff. The average concentrations of the metals are in the order of Co (0.315) > Mn (0.301) > Cr (0.291) > Zn (0.132) > Cu (0.106) > Pb (0.051) > Ni (0.050) > Cd (0.007).

Concentration of Fe is more than 6 times that of the next most abundant element, Co.

(e) The metal contamination of the runoff may be attributed to leaching from the top layers of soil which has served as a receptor for various wastes generated by anthropogenic activities in the rapidly urbanized city. Increase in traffic volume, congestion, increased fuel use might have contributed significantly to runoff contamination.

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