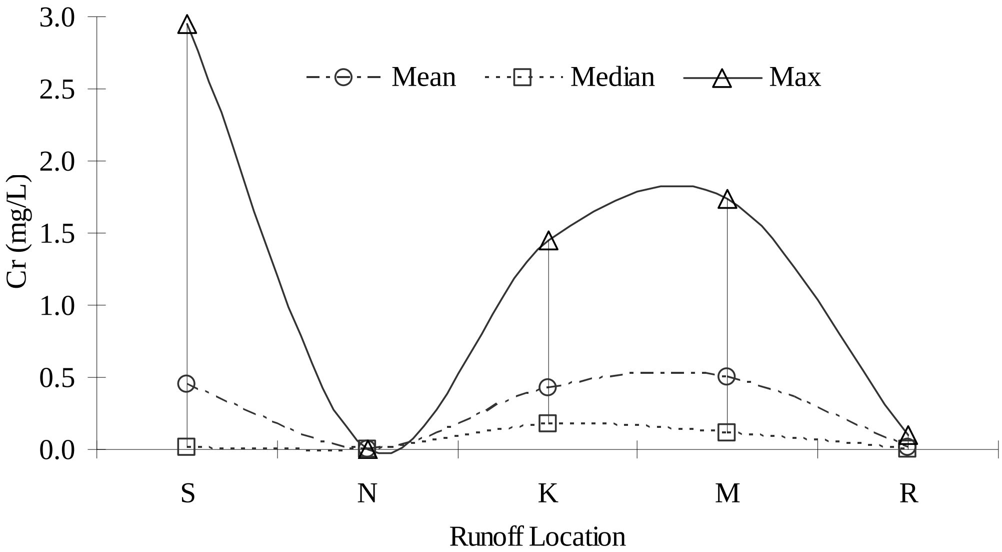

Fig. 5 Variation in the concentrations of Chromium in the runoff

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.

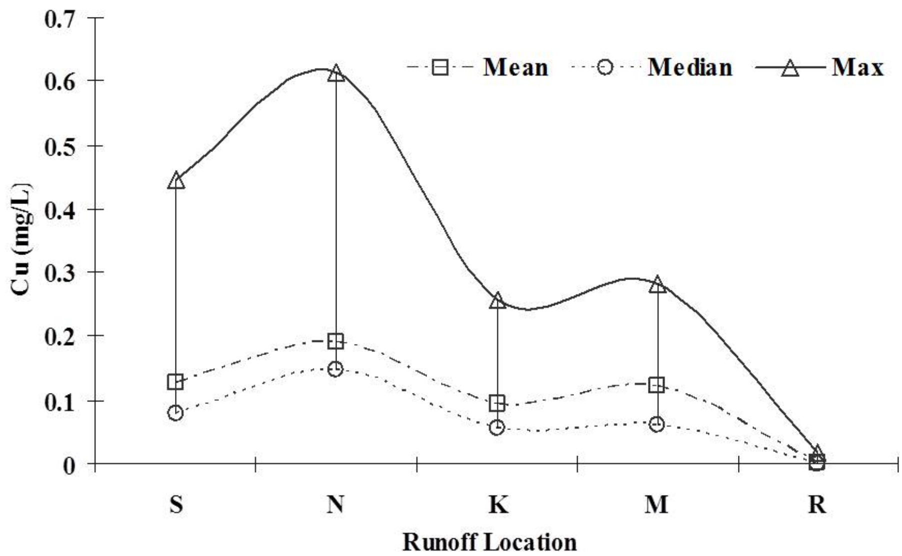

Fig. 6 Concentration of Copper in the runoff and its variation

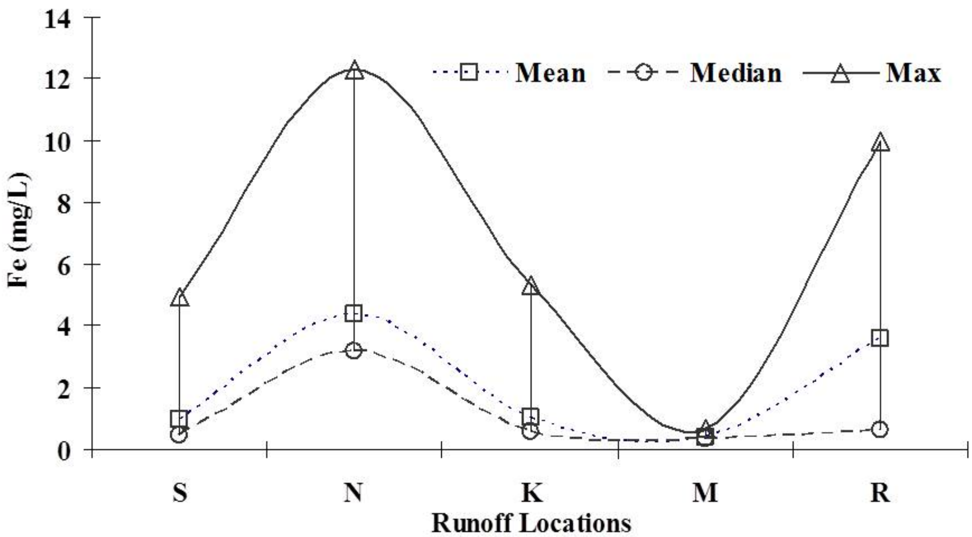

Fig. 7 Variation in the concentration of Iron in the runoff

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,

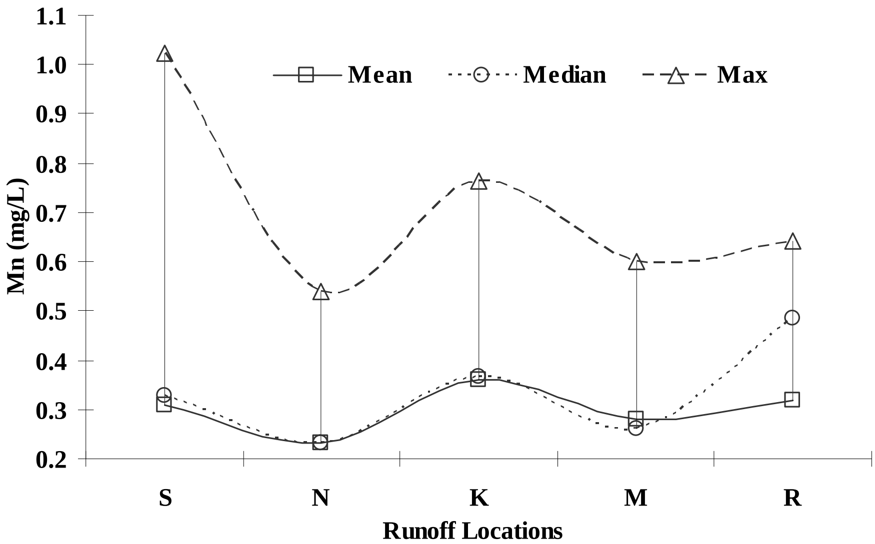

Fig. 8 Concentration of Mn in the runoff and its variations

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,

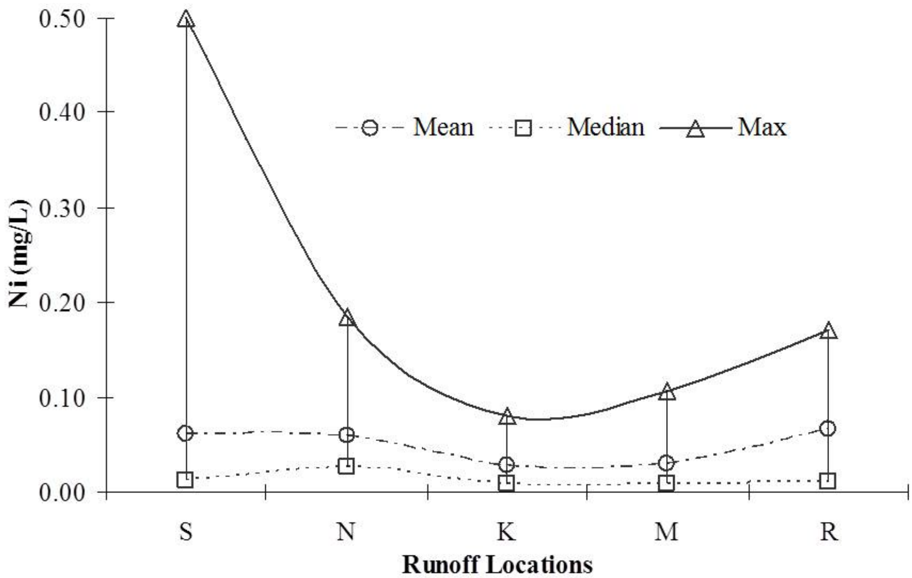

Fig. 9 Concentration variations for Nickel in the runoff

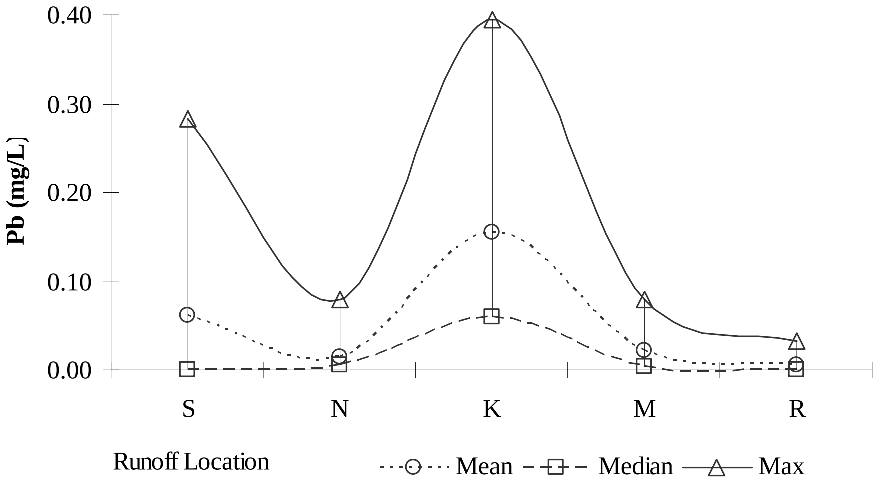

Fig. 10 Variations in Pb concentrations in the runoff

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

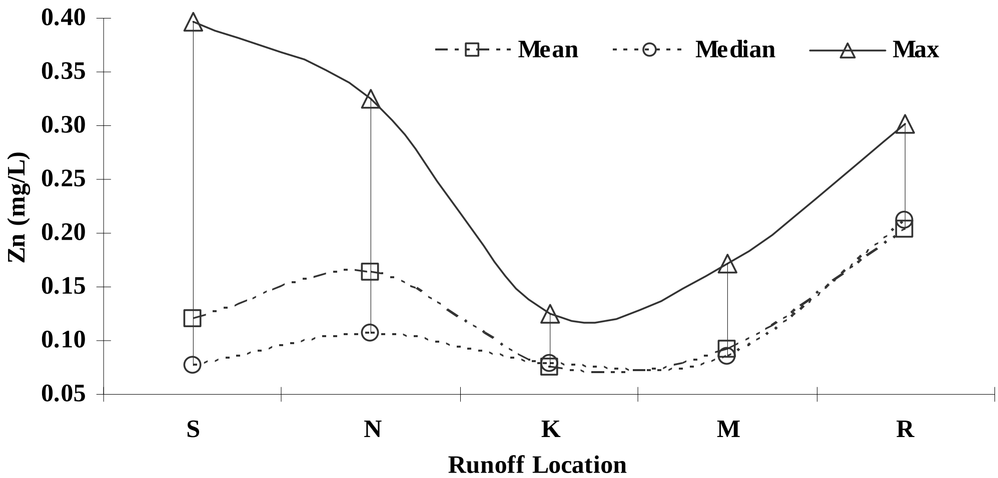

Fig. 11 Concentration of Zn in the runoff and its variation

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.

References

Adriano, D.C. (1989), *Trace Elements in the Terrestrial Environment*, (2nd Edition), Springer-Verlag, New York.

APHA (1995), *American Public Health Association, Standard Methods for the Examination of Water and Wastewater,* (19th Edition), Washington, D.C.

Avudainayagam, S., Megharaj, M., Owens, G., Kookana, R.S., Cittleborough, D. and Naidu, R. (2003), "Chemistry of chromium in soils with emphasis on tannery waste sites", *Rev. Environ. Contaminat. Toxicol.*, **178**, 53-91.

Brown, G.H., Sharp, M. and Tranter, M. (1996), "Experimental investigations of the weathering of suspended sediment by Alpine glacier meltware", *Hydrol. Process.,* **10**, 579-597.

Cezary, K. and Singh B.R. (2001), "Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter", *J. Environ. Qual.*, **30**(2), 485-492.

Charlson, R.J. and Rodhe, R. (1982), "Factors controlling the acidity of natural rainwater", *Nature*, **295**, 683-685.

Dasch, J.M. and Wolff, G.T. (1989), "Trace inorganic species in precipitation and their potential use in source apportionment studies", *Water, Air, Soil Pollut.*, **43**(3-4), 401-412.

Davis, B. and Birch, G. (2010), "Comparison of heavy metal loads in stormwater runoff from major and minor urban roads using pollutant yield rating curves", *Environ. Pollut.*, **158**(8), 2541- 2545.

Davis, A.P. and Shokouhian, M. (2001), "Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources", *Chemosphere*, **44**(5), 997-1009.

Davis, B. and Birch, G. (2010), "Comparison of heavy metal loads in stormwater runoff from major and minor urban roads using pollutant yield rating curves", *Environ. Pollut.*, **158**, 2541- 2545.

Dorchin, A. and Shanas, U. (2010), "Assessment of pollution in road runoff using a Bufo viridis biological assay", *Environ. Pollut.*, **158**, 3626-3633.

Edwards, A.C. and Withers, P.J.A. (2008), "Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK", *J. Hydrol.*, **350**(3-4), 144-153.

Facchinelli, A., Sacchi, E. and Mallen, L. (2001), "Multivariate statistical and GIS-based approach to identify heavy metal sources in soils", *Environ. Pollut.*, **114**(3), 313-324.

Farm, C. (2002), "Metal sorption to natural filter substrates for storm water treatment-column studies", *Sci. Total Environ.*, **298**(1-3), 17-24.

Forstner, U. and Wittmann, G. (1979), *Metal Pollution in the Aquatic Environment*, (2nd Revised Edition), Springer-Verlag Berlin, Heidelberg et New York, 486.

Gikas, G.D. and Tsihrintzis, V.A. (2012), "Assessment of water quality of first-flush roof runoff and harvested rainwater", *J. Hydrol.*, **466-467**(12), 115-126.

GMDA (2007), "Master plan for Guwahati Metropolitan Area-2025 (Draft)", Document: 20003139 /UP/DFR/RI/

Hesterberg, D., Bril, J. and Castilho, P.D. (1993), "Thermodynamic modelling of zinc, cadmium, and copper solubilities in manured acidic loamy-sand topsoil", *J. Environ Qual*, **22**(4), 681-688.

Hewitt, C.N. and Rashed, M.B. (1990), "An integrated budget for selected pollutants for a major rural highway", *Sci. Total Environ.*, **93**, 375-384.

Johnson, J., Schewel, L. and Graedel, T.E. (2006), "The contemporary anthropogenic chromium cycle", *Environ. Sci. Technol.*, **40**(22), 7060-7069.

Koljonen, T., Lahermo, P. and Garlson, L. (1976), "Origin mineralogy and geochemistry of manganese rocks and ferruginous precipitates found in sand gravel deposits in Finland", *Bull. Geol. Soc.*, **48**, 111-135.
Lee, H., Lau, S.L., Kayhanian, M. and Stenstrom, M.K. (2004), "Seasonal first flush phenomenon of urban storm water discharges", *Water Res*., **38**(19), 4153-4163.
Lind, C., Hem, J, and Roberson, C. (1987), "Reaction products of manganese-bearing waters", *Chem. Qual. Water Hydrol. Cycle*, 272-301.
Longhurst, R.D., Roberts, A.H.C. and Waller, J.E. (2004), "Concentrations of arsenic, cadmium, copper, lead and zinc in New Zealand pastoral topsoils and herbage", *New Zealand J. Agr. Res*., **47**(1), 23-32.
McDowell, R.W. (2010), "Is cadmium loss in surface runoff significant for soil and surface water quality: A study of flood-irrigated pastures?", *Water Air Soil Pollut*., **209**(1-4), 133-142.
Melidis, P., Akratos, C., Tsihrintzis, V.A. and Trikoilidou, E. (2007), "Characterization of rain and roof drainage water quality in Xanthi, Greece", *Environ. Monit. Assess*., **127**(1-3), 15-27.
Mermut, A.R., Jain, J.C., Song, L., Kerrich, R., Kozak, L. and Jana, S. (1996), "Trace element concentration of selected soils and fertilizers in Saskatchewan, Canada", *J. Environ. Qual*., **25**(4), 845-853
Mitchell, A., Brown, G.H. and Fuge, R. (2001), "Minor and trace elements export from a glacierised Alpine headwater catchment, Haut Glacier d' Arolla, Switzerland", *Hydrol. Process*., **15**(18), 3499-3524.
Moore, J.W. (1991), *Inorganic contaminants of surface water*, Research and Monitoring Priorities, Springer-Verlag, New York, 98-108.
Mugica, V. and Maubert, M. (2002), "Temporal and spatial variations of metal content in TSP and PM10 in Mexico City during 1996-1998", *J. Aerosol Sci*., **33**(1), 91-102.
Nagpal, N.K. (2004), "Technical report - Water Quality Guidelines for Cobalt".
Pellerin, C. and Booker, S.M. (2000), "Reflections on hexavalent chromium: Health hazards of an industrial heavyweight", *Environ. Health Perspect*., **108**(9), 402-407.
Poulton, S.W. and Raiswell, R. (2005), "Chemical and physical characteristics of iron oxides in riverine and glacier meltware sediments", *Chem. Geol*., **218**(3-4), 203-221.
Prendez, M. and Carrasco, M.A. (2003), "Elemental composition of surface waters in the Antarctic Peninsula and interactions with the environment", *Environ. Geochem. Health*, **25**(3), 347-363.
Ramesh, R. and Anbu, M. (1996), *Chemical Methods for Environmental Analysis – Water Sediment*, Macmillan Publishers, London, 33-36.
Sedlak, D.L., Phinney, J.N. and Bedsworth, W. (1997), "Strongly complexed Cu and Ni in wastewater effluents and surface runoff", *Environ. Sci. Technol*., **31**(10), 3010-3016.
Sharp, M., Tranter, M., Brown, G.H. and Skidmore, M. (1995), "Rates of chemical denudation and CO_2 drawdown in a glacier-covered alpine catchment", *Geology*, **23**(1), 61-64.
Skidmore, M., Sharp, M. and Tranter, M. (2004), "Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: Implications for detection of microbial CO_2 signatures using d13C-DIC", *Geochimica Cosmochimica Acta*, **68**(21), 4309-4317.
Tebbutt, T.H.Y. (1983), "Relation between natural water quality and health", Paris, UNESICO.
Tranter, M., Sharp, M.J., Lamb, H.R., Brown, G.H., Hubbard, B.P. and Willis, I.C. (2002), "Geochemical weathering at the bed of Haut Glacier d' Arolla, Switzerland", *Hydrol. Process*., **16**(5), 959-993.
Turer, D., Maynard, J.B. and Sansalone, J.J. (2001), "Heavy metal concentration in soils of urban highways: Comparison between runoff and soil concentrations at Cincinnati, Ohio", *Water Air Soil Pollut*., **132**, 293-314.
Tsihrintzis, V.A. and Hamid, R. (1997), "Modelling and management of urban stormwater runoff quality: A review", *Water Resour. Manag*., **11**(2), 137-164.
Vijayaraghavan, K., Joshi, U.M. and Balasubramanian, R. (2012), "A field study to evaluate runoff quality from green roofs", *Water Res*., **46**(4), 1337-1345.
Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G. and Pigna1, M. (2010), "Mobility and bioavailability of heavy metals and metalloids in soil environments", *J. Soil Sci. Plant Nutr*., **10**(3), 268-292.
Vuori, K.M. (1995), "Direct and indirect effects of iron on river ecosystem", *Ann. Zool. Fennici*, **32**,

317-329.
Zhao, H., Li, X., Wang, X. and Tian, D. (2010), "Grain size distribution of road-deposited sediment and its contribution to heavy metal pollution in urban runoff in Beijing, China", *J. Hazard. Mater.*, **183**(1-3), 203-210.

CC