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Factor analysis and linear regression model (LRM) of metal speciation and physico-chemical characters of groundwater samples

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Abstract An approach is described for viewing the interrelationship between different variables and also tracing the sources of pollution of groundwater of north Chennai (India). The data set of 43 variables which include major ions, minor ions and trace metal speciation (Cu, Pb, Cd and Zn) collected during the pre-monsoon and post-monsoon seasons of the year 2000–2001, was subjected to R-mode factor analysis to comprehend the distribution pattern of the said variables. It was found that first factor measures salinity and hardness which explained 19.12% of the total variance (comprised of variables EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, total hardness, Cl^- and SO_4^{2-}) during pre-monsoon, while it was 25.08% during post-monsoon. The second and third factors were attributed to speciation of zinc and copper ions during both pre-monsoon and post-monsoon. Although there were two more factors, loaded with speciation parameters of lead and cadmium, the variance of them were less than 10%. From this study it is seen that sea water intrusion, municipal solid waste disposal are the identified sources of component of pollution. The importance of metal ions is taking a secondary role and the anthropogenic origin-industrial activity, is the reason in the evaluation of pollution status as they come in the second, third, fourth and fifth factors. As the trace metal speciation was grouped in separate factors, linear regression model (LRM) with correlation analysis was applied to check its validity for prediction of speciation and to apply LRM for rapid monitoring of water pollution.

Keywords Factor analysis · Groundwater · Linear regression model · Metal speciation · Physico–chemical characters

Introduction

Environmental data is strongly characterized by inherent variability. Only limited understanding of the environmental distribution of contaminants can be gained from chemical analysis (Einax et al. 1997). Statistical techniques were initially confined to collection of numerical facts. It has now come to include the analysis of data, assessment of uncertainty associated with such data, and to infer the underlying principle or mechanism. Some of the commonly utilized statistical tools in the analysis of multivariate environmental data include principle component analysis, cluster analysis, R and Q-mode factor analysis, correspondence analysis, and canonical correlation. Factor analysis is termed

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R-mode, when the concern is the interrelationship between variables, and Q-mode, when attention is devoted exclusively to interrelationship between samples. In R-mode, the principle is to reduce the number of original variables by detecting the underlying relationships (Razak and Dazy 1990).

Factor analysis has the advantage of simple and graphical explanation of the relationships observed between numerous important variables. This technique also enables the determination of the relative importance of those processes affecting the environmental quality together with their spatial and temporal variations, and ecological significance in the new variables (defined as linear combinations of the variables measured in such studies). This is a valuable knowledge, since the measurement of these interacting processes is considerably more complex than the mere monitoring of the environmental variables of any system.

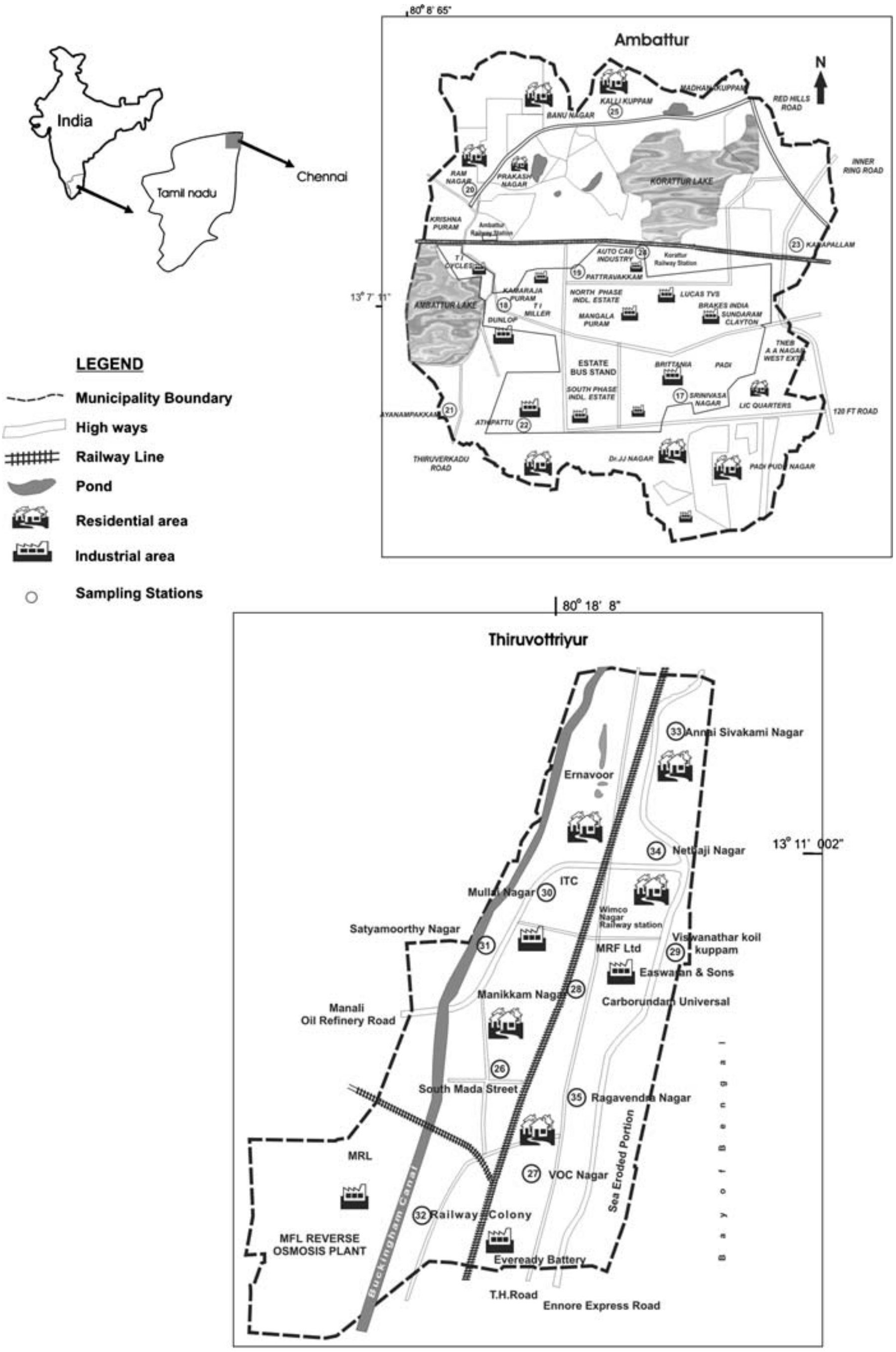
For instances, defining groundwater flow paths of Nubian Sandstone aquifer beneath the Sinai Peninsula, Egypt and the Negev Desert, Israel (Melloul 1995); the characterization of effluent contamination of groundwater of two industrial sites of Visakhapatnam, India (Subbarao et al. 1996); characterizing the groundwater using different components namely, intruding seawater, fresh water from rainfall infiltration and saline water with a characteristic sulphate-calcium-magnesium facies for Castellon Plain aquifer, Spain (Morell et al. 1996); evaluating the Rybnik Reservoir, Poland by naming, geo-accumulation index, enrichment factor, and contamination factors (Krzysztoz et al. 1997); analyzing the trace groundwater circulation in volcanic terrains using PCA based on both structural and hydrochemical parameters of 243 springs of Reunion, Western Indian Ocean (Join et al. 1997); measuring the first factor 'salinity, hardness and alkalinity' while second factor as 'pollution' for major ions of groundwater of Chennai (Ballukraya and Ravi 1999); assigning the components as 'natural' mineralization, 'saline' man-made contamination (sodium and chloride) for an alluvial aquifer of the Pisuerga River, Spain (Helena et al. 2000); terming the first component for 'physico-chemical water sample property' and further components as majority metals (Fe, Cu, Mn, Zn) and minority metals (Pb, Ni, Co, Cd) for Odiel River, Huelvo, Spain (Montes-Botella and Tenoria 2003); terming the factors, seawater salinization (factor 1), arsenic pollutant (factor 2) for a the groundwater of Blackfoot disease area of Yun-Lin, Taiwan (Liu et al. 2003); terming the factors as eutrophication factor (factor 1), copper contamination factor (factor 2), metal removal factor (factor 3), anthropogenic factor (factor 4), zinc contamination factor (factor 5) for coastal environmental system of Ennore (Kuppusamy and Giridhar 2006) are all studies on similar lines. However in the groundwater chemistry, factor analysis of metal speciation has not been reported.

The objective of the present work is to view the interrelationship between different variables of a typical set of data (3,010) including trace metal speciation using factor analysis, and to trace the sources of pollution, in this case obtained from groundwater of north Chennai, India. Speciation analysis of an element is the determination of individual physico-chemical forms of that element, which together make up its total concentration in a sample. The individual physico-chemical forms may include particulate matter and dissolved forms such as simple inorganic species, organic complexes and the elements adsorbed on a variety of colloidal particles. Labile metal consists of free metal ions and metal ions that can dissociate in the double layer from complexes and colloidal particles, and thereafter, deposited on the mercury electrode. (Florence 1986) The difference between the total and labile metal is called non-labile metal. In the present study, R-mode factor analysis was performed to comprehend the distribution patterns of major and minor ions, and trace metal speciation in groundwater of north Chennai. The R-mode has been chosen as it has several positive features in interpreting geochemical data (Lawrence and Upchurch 1982).

Description of study area

The study area Chennai, a coastal city and fourth largest city in India, lies between latitudes 12° 57′30″N and 13°8′50″N and longitudes E80° 12′10″E and 80° 18′20″E and forms part of survey of India, Topographical Maps number 66 c/4, 66 c/8, 66 d/1 and 66 d/5 covers an area of about 172 km^2. Chennai has more than 1,400 factories. Most of these factories, are situated in the northern part of Chennai, particularly Manali, Ennore, Ambattur and Thiruvottriyur. The major groups of industries are those that generate electricity (35%), manufacture rubber, plastics, purify petroleum and coal products (9.5%), transport of equipment (9.5%), machinery and machine tools (9.3%), paper and paper products (5.5%), metal products (5%) and the rest (27%). Figures 1 and 2 show the various industries: metal works (Ti Cycle, Brakes India, Lucas TVS, Sundaram Clayton , Ashok Leyland, Ennore Foundries), petroleum and fertilizer industries(MFL, MPL, SPIC, CPCL, TNPPL, IOC, B&L , Kothari fertilizer, EID Parry (I) Ltd), other industries like Ennore thermal power station, Madras Rubber Factory, Dunlop Rubber, Vimco matches and battery, pigments and dye industries.

Fig. 1 Map of the study areas Ambattur and Thiruvottriyur of North Chennai



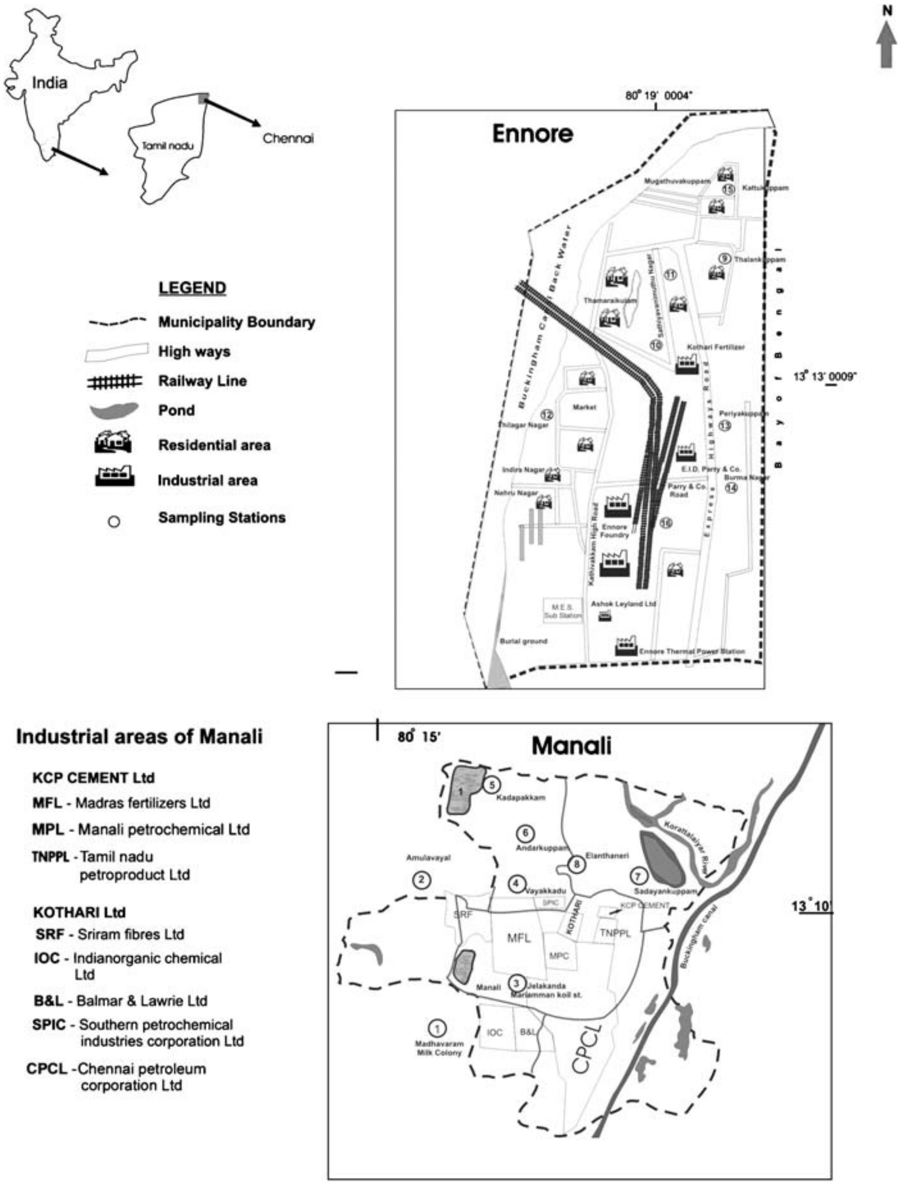


Fig. 2 Map of the study areas Ennore and Manali of North Chennai

Earlier studies carried out in Chennai focused - hydrogeology of Chennai City aquifer (Ballukraya and Ravi 1995); groundwater chemistry with respect to major and trace element (Ramesh et al. 1995); spatial and seasonal variations in heavy metals in Ennore (Rajathy and Azariah 1996); factor analysis of major ions of groundwater (Ballukraya and Ravi 1999); physico-chemical and geochemical studies in Pulicat Lake, Ennore (Padma and Periakali 1999). These studies however, do not attempt metal speciation of groundwater. Groundwater samples collected seasonally, pre-monsoon and post-monsoon, during 2000–2001 from north Chennai are selected for present study.

Materials and methods

For factor analysis, eight samples were collected from each of the study areas namely Manali and Ennore, whereas the samples 9 and 10 were collected from Ambattur and Thiruvottiyur, respectively (Figs. 1 and 2). The locations included both dug well and bore well and the interval between the sampling stations was maintained from 50 to 150 m and the samplings were as per the procedure described by Kebbekus and Mitra (1998 p. 45). As per the meteorological department, the study area received 899.2 mm of rainfall during the study year, the monsoon period of which saw 395.2 mm. The flow chart of speciation and physico-chemical analysis is represented in Fig. 3. The collected water samples were filtered immediately through a preweighed acid washed 0.45 μm pore size HA type membrane filter and the filtrates were stored at 4°C for speciation studies (Florence 1986). The particulate matter on the membrane filters were stored in clean plastic petridishes for further analysis. The differential pulse anodic stripping voltammetry (DPASV) was used to determine the concentration of trace metals like Cu, Pb, Cd and Zn in both dissolved phase and suspended particulate phase. The speciation of these metals was restricted to labile and non-labile discrimination.

Analytical procedures

The analysis of different water quality parameters like dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), alkalinity, acidity, total hardness (TH), Ca^{2+}, Mg^{2+}, Na^+, K^+, F^-, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-}.P, silica and chemical oxygen demand (COD) were determined as given in standard methods (American Public Health Association 1998). The total metal ion concentration of Fe, Co, Ni, Cr and Mn were determined using atomic absorption spectrometry (AAS). The ion-balance-error computation, taking the relationship between the total cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and the total anions (CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^-) for each set of complete analyses of water sample, is observed to be within the range of acceptability (±5%) used in most laboratories (Domenico and Schwartz 1990).

The DPASV were carried with EG&G PAR Electrochemical system (Model 273A) and SMDE (Model 303A) set up consists of hanging mercury drop electrode (working electrode), silver/silver chloride/saturated potassium chloride solution (reference electrode) and platinum wire (counter electrode). The system was kept in a horizontal Laminar flow unit (Class 100), Atlantics, India and the measurements were done, under the clean laboratory condition. For the determination of total dissolved metals, the filtered groundwater samples were irradiated with 1,000 W UV light (UV oxidation unit, Model HAPR-HP 1000, HEBER, Chennai) in acid-cleaned, Milli Q-water rinsed and dried quartz tubes in the presence of H_2O_2 and HNO_3, for 5 h to remove the dissolved organic ligands (Batley and Florence 1976). Standard addition method and DPASV were used to determine the concentrations of total dissolved metals. The

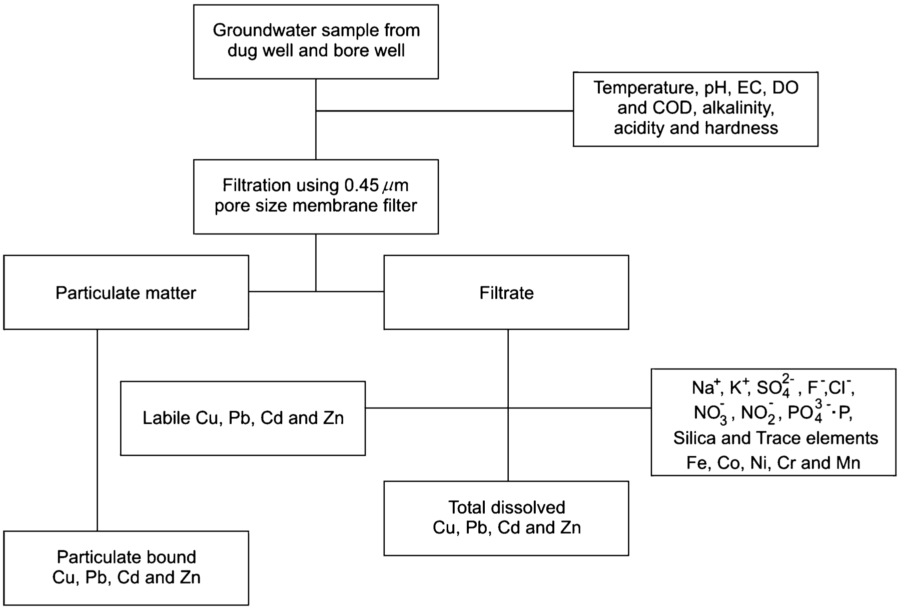


Fig. 3 Flow chart of speciation and physico-chemical analysis of groundwater collected from North Chennai

metals of interest (Cu, Pb, Cd, and Zn) were first deposited on the medium-size drop of Hg under stirred condition from the HMDE setup at −1.2 V (vs. Ag/AgCl saturated KCl) after removing oxygen from the solution by purging high pure nitrogen for 5 min. After deposition, the stirring was automatically stopped and equilibrated for 15 s. During stripping, the potential was changed from −1.2 to 0 V at a scan rate of 5 mV/s with a pulse amplitude of 50 mV. The stripping peaks for these metals occurred around −1.2 V (Zn), −0.8 V (Cd), −0.6 V (Pb) and −0.1 V (Cu). The linearity of calibration curve by DPASV was separately tested using aqueous metal standards (E. Merck) after suitable dilutions. The analysis of the labile metal was carried out at pH 4.7 without UV irradiation of the sample (Florence 1986). 5.0 ml each of filtered water sample and 0.025 M acetate buffer were transferred to the quartz voltammetric cell and the labile metal measurements were performed as described earlier, by DPASV. The non-labile metal was calculated by difference.

The suspended particulate matter collected on the filter paper during filtration was dried at 80°C. The suspended particulate matter-bound trace metals were analyzed by DPASV following the procedure of De Luca Rebello et al. (1986).

Statistical analysis

The experimental data were analysed using Statistical Package for Social Sciences (SPSS) version 6.2 for factor analysis. Extraction of the factors was carried out by principal component analysis (PCA). The output data from this study gives the univariate statistics corresponding to the total samples analyzed, eigenvalues for different factors, % variance accounted, cumulative % variance, correlation matrix, scree plot, component loadings (un-rotated and rotated) and factor scores. In order to decide upon the number of components those with eigenvalue >1 was taken. Varimax rotation was done in order to obtain the component loadings concentrated on any one of the factor axes. The objective of this analysis is primarily to create an entirely new set of variables (read factors) much smaller in number to partially or completely replace the original data set of variables for inclusion in subsequent analysis.

Results and discussion

In the factorial analysis applied to 43 variables measured at the 35 sites during pre- monsoon, five factors were obtained that occurs for 62.81% of the total variance of the data (Table 1).

Factor 1

The high loading (factor score >0.5) is observed for major ions namely EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, TH, Cl^- and SO_4^{2-} and these account for 19.12%. This factor invariably indicated that the TDS in the study area was mostly contributed by the said cations. The association of EC was known for obvious reasons. This factor measures high salinity (Na^+, Cl^-, K^+) and hardness (Ca^{2+}, Mg^{2+}, TH, SO_4^{2-}). Figures 4 and 5 show the chemical data of the groundwater samples collected from the study area plotted in the Piper's diagram (Piper 1953), indicating that 'Na' type of water predominated in all the four areas except Ambattur, as it is comparatively away from coastal line and so seawater intrusion is minimum. Pollution due to salt water intrusion from the sea is reported in Manali area (Swaminathan and Narayanan 1994). After the rain, there is a change in hydrochemical facies, i.e., 'Na' type to 'No dominant' type, due to increase in solubility of calcium and magnesium minerals during rainfall, which is revealed from subdivision of the diamond 2 - 'alkalies exceed alkaline earths' which dominated during pre-monsoon, whereas during post-monsoon, subdivision 1 - 'alkaline earths exceed alkalies,' dominated. Sea water intrusion in Chennai is further supported by geo-electrical measurements using vertical electrical sounding (VES) method (Gnansundar and Elango 1999). The factor analysis study, viz., sector of Coastellon, plain aquifer, Spain (Morell et al. 1996), groundwater of Blackfoot disease area, Taiwan (Liu et al. 2003), and Deltic Plain sands Aquifer of Warri, Nigeria (Olobaniya and Owoyemi 2006) reflect the signature of saline water intrusion. The potential sources of anthropogenic sources of SO_4^{2-} include industrial discharge, domestic sewage, urban and road drainage and atmospheric deposition (Nriagu 1978). According to Somasundaram et al. (1993), the dump of 3,000 tons per day of full range of domestic and industrial garbage within the Chennai City resulted in the high chloride ion, SO_4^{2-} in groundwater.

Table 1 Results of factor analysis during pre-monsoon period

Variables	Factors				
	1	2	3	4	5
Water Column depth	−0.124	−0.021	0.318	−0.317	−0.049
Temperature	0.246	−0.088	0.154	−0.157	−0.372
PH	0.386	0.079	−0.331	−0.390	0.123
EC	**0.970**	−0.064	−0.075	−0.004	−0.014
Na^+	**0.812**	−0.042	−0.062	−0.044	−0.056
K^+	**0.579**	−0.061	0.084	0.208	0.028
Ca^{2+}	**0.872**	−0.176	−0.047	0.023	0.017
Mg^{2+}	**0.903**	0.108	−0.113	0.016	0.024
TH	**0.952**	−0.037	−0.088	0.017	0.017
F^-	−0.016	−0.033	0.442	0.079	−0.119
Cl^-	**0.961**	−0.110	−0.124	0.024	−0.013
SO_4^{2-}	**0.515**	0.046	−0.0003	−0.071	0.052
NO_3^-	0.105	0.257	0.245	−0.057	−0.041
NO_2^-	0.006	−0.164	0.290	0.052	0.119
PO_4^{3-}.P	−0.14	−0.290	−0.295	−0.235	0.133
HCO_3^-	0.270	−0.025	0.155	−0.007	−0.121
SiO_2	−0.042	−0.130	0.168	0.118	0.087
Acidity	0.067	0.156	−0.021	−0.094	−0.084
DO	0.022	**−0.622**	−0.283	−0.155	0.356
TDS	**0.962**	−0.065	−0.059	0.004	0.003
TSS	−0.095	**0.877**	−0.022	0.004	0.134
COD	−0.000	**0.881**	0.248	0.099	−0.006
Fe	−0.179	−0.067	−0.170	0.034	0.026
Co	0.045	0.006	−0.183	−0.179	**0.658**
Ni	0.271	0.123	−0.087	0.099	−0.020
Mn	0.138	0.063	−0.029	0.119	0.125
LCu	−0.167	−0.083	**0.884**	−0.015	−0.123
Nl-Cu	−0.101	0.004	**0.963**	0.011	−0.073
Td-Cu	−0.119	−0.017	**0.964**	0.000	−0.085
Pt-Cu	−0.071	−0.029	**0.923**	0.036	−0.036
L-Pb	−0.063	−0.001	−0.104	**0.861**	−0.113
Nl-Pb	0.021	0.121	0.126	**0.933**	0.176
Td-Pb	0.035	0.088	0.059	**0.962**	0.093
Pt-Pb	−0.067	0.345	−0.089	**0.637**	0.042
L-Cd	0.217	−0.155	−0.127	0.204	0.260
Nl-Cd	−0.038	−0.151	−0.069	0.119	**0.947**
Td-Cd	0.083	−0.189	−0.115	0.191	**0.823**
Pt-Cd	−0.060	−0.060	0.351	0.138	0.063
L-Zn	−0.045	**0.957**	−0.089	0.049	−0.133
Nl-Zn	−0.035	**0.966**	−0.096	0.083	−0.099
Td-Zn	−0.038	**0.967**	−0.094	0.072	−0.110
Pt-Zn	−0.104	**0.832**	−0.110	0.029	−0.021
Total Eigen values	8.030	6.317	4.925	4.124	2.986
% of variance	19.12	15.04	11.73	9.82	7.11
Cumulative %	19.12	34.16	45.89	55.70	62.81

Bold denotes significant scores. Extraction method: Principal component analysis. Rotation method: Varimax with Keizer Normalization.

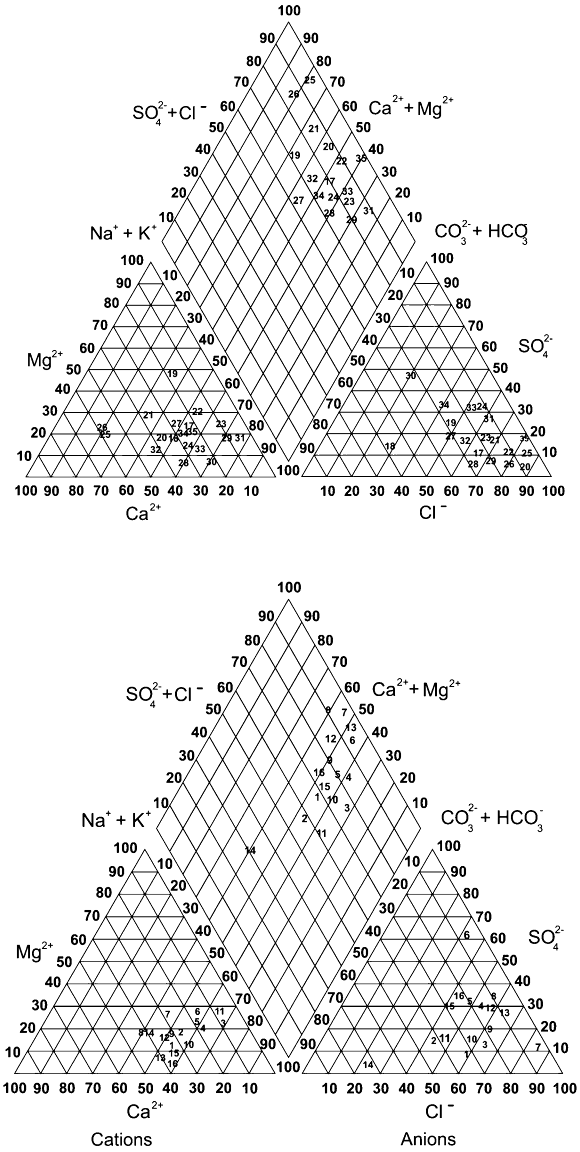


Fig. 4 Piper tri-linear diagram of groundwater of North Chennai during pre-monsoon (Numbers 1–35 indicating the sampling station)

Factor 2

The second factor contributed 15.04% of the variance and had positive loading on TSS, COD, labile zinc (L-Zn), non-labile zinc (Nl-Zn), total dissolved zinc (Td-Zn), particulate zinc (Pt-Zn) and negative loading on dissolved oxygen (DO). All the zinc related parameters grouped in this factor was engaged by significant correlation coefficient value (Table 3). The relationship 'as COD increases DO decreases' is revealed in this factor. The zinc ion speciation was grouped together along with TSS. It was riveted that particulate zinc was contributing more to TSS rather than other trace metals in the system. From the estimates of anthropogenic emissions of zinc given by Nriagu (1990) and Nriagu and Pacyna (1988), it is very clear that the manufacturing processes (metal, chemical, petroleum products) is the highest contributor (85,000 tons/year) to the world-wide atmospheric emissions of zinc from anthropogenic sources, while domestic waste is second in line (48,000 tons/year). Nriagu (1990) also mentions that anthropogenic emissions of zinc far exceed those from natural

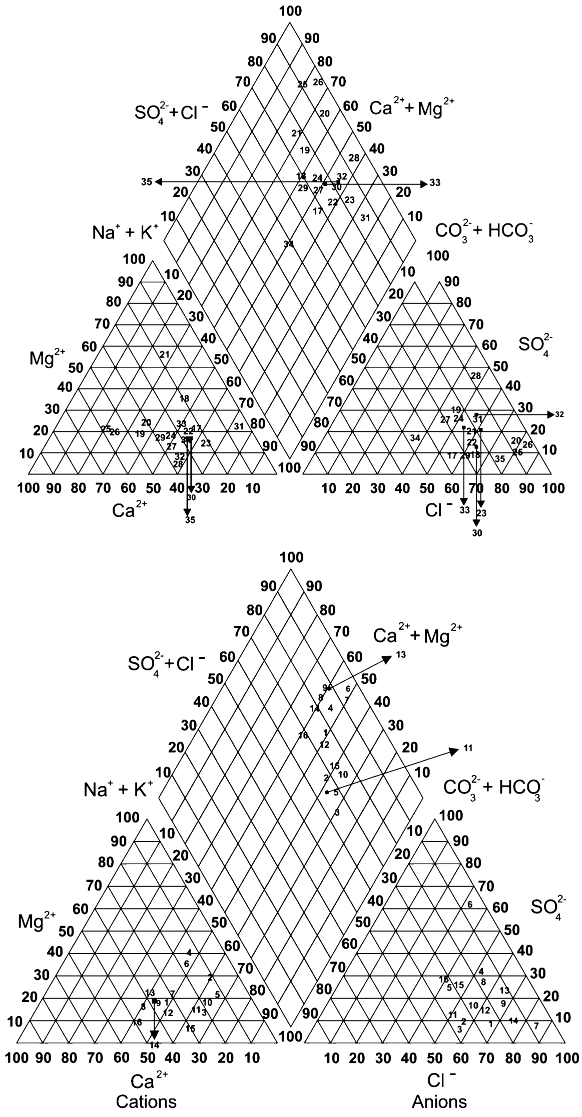


Fig. 5 Piper tri-linear diagram of groundwater of North Chennai during post-monsoon (Numbers 1–35 indicating the sampling station)

sources. The study area also comprises of industries based on metal works and petrochemical, which may be contributing to anthropogenic zinc. Buckingham canal running across the study area contains highly polluted liquid waste. According to Sahayadas and Azariah, (1997) Buckingham canal has 122 pollution outfalls and discharging of industrial effluents of Manali into this canal had been reported (Bonofer 2004). A significant part of anthropogenic zinc was emitted to the environment and transported to air, soil, sediments, rivers and related ecosystems, along with particulate matter, sewage sludge, effluents. Consequently enrichment of zinc occurred in receiving systems. Rajathy and Azariah (1996) pointed that the heavy metals namely zinc, copper in the sediment and water bodies of industrial region of Ennore exceeded the admissible limit. Weerasooriya et al. (1983) noted that the contaminated city canal of Colombo by Zn, Pb, Cd due to industry is the obvious reason for the contaminated drinking water wells. The heavy metal pollution in environmental samples due to industries of metal works was further supported by the study at Golden Horn, Turkey (Tuncer et al. 2001), Alia Image metal industry district, Zamir City, Turkey (Sponza and Karaoglu 2002).

Factor 3

The high positive loading on L-Cu, Nl-Cu, Td-Cu and Pt-Cu resulted as third factor and contributed to 11.73% of the variance. All the parameters related to copper were grouped in this factor from which it was inferred that there were some interassociation of copper ion speciation, which either increases or decreases. The origin for copper contamination is anthropogenic sources. Similar to atmospheric zinc emission, the value contributed for copper by the manufacturing processes is 34,000 tons/year, while domestic waste is second in line with 28,000 tons/year. This makes it clear that the metal works, petroleum and fertilizer industries of the study area are the ones emitting copper ion. Kuppusamy and Giridhar (2006) noticed that the industrial waste dumping from Manali industrial area and Buckingham Canal discharges into Ennore estuary was the reason for copper contamination, during his study from 1998 to 2000. Also, Ramesh et al. (1995) pointed out that trace elements in groundwater of Chennai is of anthropogenic origin and he termed the factors as ‘pollution’ and ‘mobilization factor.’

Factor 4

Factor 4, which contributed to 9.82% of the variance, had positive loading on L-Pb, Nl-Pb, Td-Pb, and Pt-Pb. All the speciation of lead ion is associated in this factor. According to Nriagu (1990) the world-wide inputs of lead into aquatic system is mainly due to atmospheric fall-out (100,000 tons/year), while manufacturing processes contribute only to 14,000 tons/year. The anthropogenic sources for lead pollution in the study area are automobile emission and industrial activities of fertilizers, battery, pigments and dye. As it is supported that Eick et al. (1999) summarized the main sources of Pb pollution are exhaust fumes of automobiles, chimneys of factories using Pb, effluents from the storage battery, mining and smelting of Pb ores, metal plating and finishing operations, fertilizers, pesticides and additives in pigments and gasoline. Mohammad and Alam (1997) drove the point that the contamination source for the higher concentration of lead in the groundwater samples of the industrial city of Dhahran, was due to leakage from industries like the fertilizer plant. Beceiro-Gonzalez et al. 1997 reported that lead reflected a pollution pattern originating mainly by automobile exhausts in an airborne metal particulate study in a coastal city in north west Spain, while Lee et al. (2006) pointed to high traffic conditions and vehicular emission for increasing lead concentration in the urban soil of northern and western parts of Hong Kong Island. The study area, being an urban area, obviously has automobile exhaust contributing substantially to the atmospheric pollution. The lead ion may enter into the aquatic environment using different path way viz. sedimentation, rainfall containing atmospheric lead and urban storm water run-off.

Factor 5

The lowest eigenvalue component (7.11%) gives a positive loading on cobalt ion, Nl-Cd and Td-Cd. The Td-Cd was being contributed by Nl-Cd rather than L-Cd indicating its probable association with organic colloids during pre-monsoon, while during post-monsoon both L-Cd and Nl-Cd contributed to Td-Cd. The estimated (World Health Organization 1992) world-wide inputs of cadmium into soil is mainly due to coal ash (7.2) while atmospheric fall-out stands second (5.3), emissions read in thousand tons/year.

Table 2 Results of factor analysis during post-monsoon period

Variables	Factors				
	1	2	3	4	5
Water column depth	−0.217	−0.150	0.346	−0.092	−0.146
Temperature	−0.008	−0.060	−0.162	0.006	−0.436
PH	**0.646**	−0.151	−0.465	−0.074	−0.063
EC	**0.966**	0.075	0.050	0.138	0.080
Na^+	**0.870**	0.054	0.025	0.066	0.033
K^+	0.455	−0.058	0.024	0.621	0.032
Ca^{2+}	**0.870**	−0.064	−0.128	−0.122	−0.059
Mg^{2+}	**0.762**	0.201	0.227	0.319	0.260
TH	**0.931**	0.083	0.058	0.115	0.118
F^-	−0.028	−0.011	0.110	−0.137	0.023
Cl^-	**0.945**	−0.139	−0.078	0.054	0.053
SO_4^{2-}	**0.496**	0.332	0.316	0.159	0.291
NO_3^-	−0.086	0.263	0.094	0.000	−0.159
NO_2^-	0.015	0.023	0.182	−0.036	−0.116
PO_4^{3-}.P	−0.033	−0.151	−0.181	−0.010	−0.196
HCO_3^-	0.427	0.096	−0.197	0.251	−0.336
SiO_2	−0.038	−0.094	0.023	−0.060	−0.007
Acidity	0.140	−0.056	−0.144	0.344	0.101
DO	−0.005	**−0.618**	−0.336	−0.015	−0.124
TDS	**0.962**	0.071	0.045	0.172	0.072
TSS	0.038	**0.905**	0.176	−0.045	0.145
COD	0.122	**0.774**	0.285	0.107	0.077
Fe	−0.131	−0.140	−0.204	−0.045	−0.073
Co	0.389	−0.044	0.031	0.442	0.071
Ni	0.453	0.232	0.055	−0.050	0.005
Mn	0.272	0.283	0.339	0.053	0.418
L-Cu	−0.024	−0.010	**0.927**	0.034	0.045
Nl-Cu	−0.000	0.060	**0.966**	0.057	0.029
Td-Cu	0.004	0.048	**0.964**	0.054	0.023
Pt-Cu	0.027	0.121	**0.935**	0.067	0.121
L-Pb	0.112	0.208	−0.016	0.178	**0.894**
Nl-Pb	0.200	0.303	0.187	0.446	**0.701**
Td-Pb	0.176	0.281	0.122	0.389	**0.792**
Pt-Pb	−0.093	0.497	0.039	0.221	0.415
L-Cd	0.151	0.013	0.110	**0.916**	0.214
Nl-Cd	0.001	−0.076	0.014	**0.947**	0.105
Td-Cd	0.070	−0.038	0.059	**0.973**	0.159
Pt-Cd	0.010	−0.006	0.081	0.453	0.128
L-Zn	−0.047	**0.957**	−0.084	−0.113	0.056
Nl-Zn	0.014	**0.973**	−0.041	−0.006	0.110
Td-Zn	−0.005	**0.976**	−0.055	−0.042	0.089
Pt-Zn	0.061	**0.941**	0.023	−0.012	0.086
Total Eigen values	10.534	6.908	4.598	3.708	2.947
% of variance	25.08	16.45	10.95	8.83	7.02
Cumulative %	25.08	41.53	52.48	61.31	68.32

Bold denotes significant scores. Extraction method: Principal component analysis. Rotation method: Varimax with Keizer Normalization.

The coal fire power station environmental impact study was carried out at New Delhi, India (Mehra et al. 1998) and at Illionois, USA (Paul et al. 1998) causing the leaching of trace metal cadmium into groundwater. The identified source is fire thermal power plant of Ennore. As Padma and Periakali (1999) puts it - burning of coal in the nearby Ennore thermal power plant contribute Cd to Pulicat Lake, east coast of India. Cobalt is one among the 15 trace elements released by the burning of coal associated in this factor (Clean Air Act Amendments 1990).

After the rain (post-monsoon), principal components explained 68.32% of the variance in the original data set (Table 2). Similar to pre-monsoon, major ions excluding K^+, zinc ion speciation with COD, DO and TSS and copper ion speciation contributed to the first, second and third factors respectively, accounting to the total variance of 25.08, 16.45 and 10.95%. A high positive loading on cadmium ion speciation except Pt-Cd grouped in the fourth factor contributed to 8.83% of the total variance. The inter association of L-Cd, Nl-Cd and Td-Cd had partially masked the influence of Pt-Cd in this factor. Similar to Cd, the lead ion speciation except Pt-Pb grouped (7% of the total variance) in the fifth factor.

Linear regression model

One of the major objectives in the global clean-up action of WHO (world health organization), is to find out strategies and analytical tools for the rapid monitoring of water pollution. This has accelerated the research activities of environmental scientists to find out analytical tools, models and methods, which will serve this purpose. It has been well established by number of researchers in the application of regression technique in water chemistry such as, the prediction of binding capacity of Pb using the concentrations of OH^-, CO_3^{2-} and SO_4^{2-} and the binding capacity of Cu using OH^- and SO_4^{2-}, in northern European surface waters (Giesy and Briese 1980); the existence of positive correlation-dissolved Cu and DOC (dissolved organic carbon) and Zn and DOC in south Francisco Bay (Kuwabava et al. 1989); the existence of significant correlations (water quality index & K^+, COD and phosphate ion, temporary hardness and permanent hardness) for the Match industry effluent of Sivakasi, India (Kannan and Vallinayagam 1992); the linear relation to predict the values of COD as a function of TSS for the effluent of Modigram Cement Limestone Mines at Modi Nagar, India (Sahoo et al.

Table 3 Correlation coefficient matrix of speciation of trace metals Cu, Pb, Cd and Zn during pre-monsoon

	L-Cu	Nl-Cu	Td-Cu	Pt-Cu	L-Pb	Nl-Pb	Td-Pb	P-Pb	L-Cd	Nl-Cd	Td-Cd	Pt-Cd	L-Zn	Nl-Zn	Td-Zn	Pt-Zn
L-Cu	1.000	0.891	0.936	0.751	−0.145	0.103	0.029	−0.072	−0.018	−0.001	−0.021	0.309	−0.149	−0.148	−0.149	−0.110
Nl-Cu		1.000	**0.994**	**0.914**	−0.062	0.117	0.066	−0.049	−0.156	−0.135	−0.178	0.415	−0.064	−0.069	−0.068	−0.074
Td-Cu			1.000	**0.893**	−0.084	0.166	0.058	−0.056	−0.164	−0.144	−0.189	−0.397	−0.087	−0.090	−0.089	−0.085
Pt-Cu				1.000	−0.050	0.139	0.086	−0.048	−0.168	−0.113	−0.168	0.396	−0.050	−0.115	−0.116	−0.057
L-Pb					1.000	**0.755**	**0.876**	0.425	0.287	−0.001	0.146	−0.312	0.090	0.080	0.084	−0.010
Nl-Pb						1.000	**0.977**	**0.558**	0.158	0.229	0.248	0.196	0.755	0.150	0.137	0.121
Td-Pb							1.000	**0.547**	0.209	0.168	0.229	0.238	0.107	0.136	0.127	0.085
Pt-Pb								1.000	0.142	0.062	0.118	−0.030	0.344	0.401	0.384	0.319
L-Cd									1.000	0.279	**0.714**	0.100	−0.118	−0.142	−0.135	−0.182
Nl-Cd										1.000	**0.871**	0.037	−0.244	−0.214	−0.224	−0.155
Td-Cd											1.000	0.078	−0.238	−0.228	−0.232	−0.206
Pt-Cd												1.000	−0.080	−0.113	−0.103	−0.096
L-Zn													1.000	**0.984**	**0.992**	**0.767**
Nl-Zn														1.000	**0.998**	**0.815**
Td-Zn															1.000	**0.802**
Pt-Zn																1.000

1997); linear regression equation correlating trihalomethane and haloacetic acids of finishing drinking waters from heterogeneous sources (Villanveva et al. 2003); linear equation relating total ionic concentration and electrical conductivity in natural aqueous systems from low to medium level salt content in Mediterranean agricultural environment (Visconti Reluy et al. 2004); simple linear relationship of truly dissolved and total filterable Cd, Cu, Ni, Zn of aquatic environment, for estimating truly dissolved element concentration in aqueous systems (Vignati et al. 2005); the documented strong predictive relationship between water quality and the landscape characteristics in the Fort Benning Military Installation, Georgia (Shirish et al. 2006); the significant correlation between Na levels in soil and in groundwater, Cr levels in soil and Ca level in groundwater of environmental samples located near tannery industry, Peshawar, Pakistan (Saadia et al. 2006).

Here in the present study, the analytical results of speciation parameters were subjected for correlation analysis by using Excel spreadsheet. The correlation coefficient values for pre-monsoon and post-monsoon are presented in the Tables 3 and 4 in the form of correlation matrix. Except a few, many correlations were found to be good to excellent, indicating that, for a particular part of an ecosystem, different parameters were strongly interrelated. The correlation coefficient exhibited during pre-monsoon was,

$$\mathrm{L-Zn}\ \mathit{Vs}\ \mathrm{Td-Zn}(\mathrm{r}=0.992),\ \mathrm{L-Cu\ vs\ Td} \\ -\mathrm{Cu}(r=0.936), \mathrm{Nl-Pb\ vs\ Td-Pb}(r=0.977) \\ \mathrm{and\ Nl-Cd\ vs\ Td-Cd}(r=0.871)$$

The correlation coefficient exhibited during post-monsoon was,

$$\mathrm{L-Zn\ vs\ Td-Zn}(r=0.985),\ \mathrm{L-Cu\ vs\ Td} \\ -\mathrm{Cu}(r=0.956), \mathrm{Nl-Pb\ vs\ Td-Pb}(r=0.992) \\ \mathrm{and\ Nl-Cd\ vs\ Td-Cd}(r=0.968)$$

The linear relationships noticed for these correlations are listed below.

Pre-monsoon

$$\mathrm{L-Cu}=2.942 \\ +0.23(\mathrm{Td-Cu})(r=0.876) \tag{1}$$

$$\mathrm{Nl-Pb}=0.093 \\ +0.720(\mathrm{Td-Pb})(r=0.957) \tag{2}$$

$$\mathrm{Nl-Cd}=0.067 \\ +0.634(\mathrm{Td-Cd})(r=0.756) \tag{3}$$

Table 4 Correlation coefficient matrix of speciation of trace metals Cu, Pb, Cd and Zn during post-monsoon

	L-Cu	Nl-Cu	Td-Cu	Pt-Cu	L-Pb	Nl-Pb	Td-Pb	Pt-Pb	L-Cd	Nl-Cd	Td-Cd	Pt-Cd	L-Zn	Nl-Zn	Td-Zn	Pt-Zn
L-Cu	1.000	**0.925**	**0.956**	**0.862**	0.020	0.236	0.171	0.080	0.128	0.068	0.099	0.073	−0.066	−0.004	−0.024	0.068
Nl-Cu		1.000	**0.994**	**0.920**	0.061	0.248	0.192	0.098	0.151	0.100	0.128	0.150	−0.012	0.047	0.028	0.111
Td-Cu			1.000	**0.917**	0.051	0.250	0.191	0.083	0.149	0.094	0.124	0.137	−0.021	0.040	0.021	0.105
Pt-Cu				1.000	0.137	0.380	0.308	0.158	0.177	0.114	0.148	0.017	0.022	0.084	0.064	0.170
L-Pb					1.000	**0.819**	**0.912**	0.342	0.368	0.260	0.321	0.267	0.227	0.312	0.282	0.260
Nl-Pb						1.000	**0.992**	0.451	**0.623**	0.496	**0.576**	0.355	0.231	0.356	0.315	0.351
Td-Pb							1.000	0.438	**0.576**	0.450	**0.527**	0.348	0.237	0.355	0.315	0.332
Pt-Pb								1.000	0.261	0.218	0.247	0.099	0.474	**0.535**	**0.520**	**0.627**
L-Cd									1.000	**0.837**	**0.948**	0.502	−0.101	0.014	−0.025	0.015
Nl-Cd										1.000	**0.968**	0.440	−0.163	−0.052	−0.090	−0.052
Td-Cd											1.000	0.487	−0.142	−0.024	−0.064	−0.024
Pt-Cd												1.000	−0.043	0.020	0.000	0.305
L-Zn													1.000	**0.968**	**0.985**	**0.906**
Nl-Zn														1.000	**0.997**	**0.940**
Td-Zn															1.000	**0.936**
Pt-Zn																1.000

$$\mathrm{L-Zn} = -0.627 + 3.138(\mathrm{Td-Zn})(r = 0.986) \tag{4}$$

Post-monsoon

$$\mathrm{L-Cu} = 1.640 + 0.240(\mathrm{Td-Cu})(r = 0.914) \tag{5}$$

$$\mathrm{Nl-Pb} = 0.021 + 0.724(\mathrm{Td-Pb})(r = 0.964) \tag{6}$$

$$\mathrm{Nl-Cd} = 0.03 + 0.562(\mathrm{Td-Cd})(r = 0.935) \tag{7}$$

$$\mathrm{L-}Zn = -0.542 + 0.336(\mathrm{Td-Zn})(r = 0.970) \tag{8}$$

The above results (Eqs. 1–8) indicated that it is enough if one water quality parameter (WQP) is known and the other WQP could be predicted. If the total dissolved metal of copper or zinc was known, L-Cu or L-Zn could be predicted from the linear equations (1) and (4) respectively. The non-labile fraction could be determined by subtracting labile fraction from total dissolved fraction. Similarly if the total dissolved metal of lead or cadmium was known, the respective non-labile fraction could be predicted from the linear equations (2) and (3) respectively. The regression equations (5)–(8) were proposed for post-monsoon period to predict L-Cu, Nl-Pb, Nl-Cd and L-Zn respectively from the respective total dissolved metal. The Eqs. 1–8 are highly useful in computing the trace metal speciation of Cu, Pb, Cd and Zn and the predicted values estimated using these equations were also linearly related to the corresponding experimental values. The correlation coefficient values obtained during pre-monsoon for the predicted vs. experimental values of L-Cu, Nl-Pb, L-Zn, Nl-Cd are 0.876, 0.956, 0.998 and 0.986 respectively and during post-monsoon it was 0.914, 0.964, 0.934 and 0.97 respectively. The present investigation indicated that, some statistically significant correlations existed among trace metal speciation of Cu, Pb, Cd and Zn of north Chennai groundwater. The LRMs could be used for the prediction of speciation data from the total metal ion concentration.

Final remarks

From the above discussions, major ions contributed to most part of the observed variance in the data and the sources responsible are seawater intrusion and municipal solid waste. Though the variables EC, TDS, Na^{+}, Ca^{2+}, Mg^{2+}, TH, Cl^{-} and SO_4^{2-} are loaded in the first factor in both the seasons, Piper's diagram revealed that, 'alkalies exceeds alkaline earths' dominated during pre-monsoon, and 'alkaline earths exceeds alkalies', dominated during post-monsoon. Speciation of zinc ion and copper ion contributed to second and third factors in both the seasons. The fractions related to lead ion and cadmium ion falling in the remaining two factors accounted for only less than 10% variance. Pt-Cd is not associated with the speciation parameters in both the seasons whereas Pt-Pb is not during post-monsoon. The metal ions contribution is anthropogenic in origin, viz. automobile emission and industries such as metal works, petrochemical, fertilizers and coal fire power plant. Thus evaluation and interpretation of large complex data sets were simplified by factor analysis and the correlation analysis aids the task of monitoring labile and non-labile fraction of Cu, Pb, Cd and Zn.

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