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Groundwater Acidification and Impact of Wastewater Infiltration on Groundwater Quality of Pune Metropolitan Region, Maharashtra, India

***A Supekar[1], N. J. Pawar[2]**

Author's Affiliations:
[1]Department of Geology, Savitribai Phule Pune University, Pune, Maharashtra 411007, India.
[2]D. Y. Patil Medical University, Pimpri, Pune, Maharashtra 411018, India.

***Corresponding Author: A Supekar**, Department of Geology, Savitribai Phule Pune University, Pune, Maharashtra 411007, India.
E-mail: ashwinis@unipune.ac.in

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ABSTRACT

Acidification is a natural process directly proportional to the rise in population. Wastewater recharge is an important contributor. Increased waste leakage is considered to be a major and obvious source of groundwater adulteration. Acidification of groundwater is commonly associated with anthropogenic activities. Anthropogenically derived pollutant deposition augments the rate of acidification, which in turn exceeds the natural neutralizing capacity. An important consequence of acidification is an increased human introduction to toxic elements via food and drinking water resulting in potentially adverse health effects (Thordarson et al., 1996). Acidification is described as the loss of nutrient bases (calcium, magnesium, and potassium) via the process of leaching and their replacement by acidic elements (hydrogen and aluminum) (Air pollution Information System). Acidification of groundwater affects the natural environment like soils, waters, flora, and fauna, it is considered to be the most serious environmental issues. Groundwater acidification severely affects the regions. A variety of factors like land use, soil characteristics, flow patterns, precipitation characteristics, and depth to the groundwater table are responsible for this process. However, weathering of parent material is the chief mode in which cations are replenished, other soil processes such as adsorption and microbial reduction of SO_4 also assist to ameliorate acidification. High concentrations of almost all major cations and anions resulting due to the infiltration of wastewater into the aquifers characterize the groundwaters in the study area. A decrease in pH values and concomitant increase in EC in the areas under intense urbanization suggest acidification of groundwater in PMR. Similarly, the positive correlations between Cl vs. NO_3, Cl vs. SO_4, and well elevation vs. ionic concentration respectively confirm the role of land use variables and topography on groundwater chemistry and anthropogenic inputs (Foppen, 2002). This study puts forward the view that groundwater acidification in PMR is a function of anthropogenic activity, topography and land-use factors.

KEYWORDS: *PMR, Urbanization, Groundwater Acidification, Anthropogenic Inputs.*

INTRODUCTION

Acidification trends

Effects of Acid deposition and acidification on soils and plants has been observed since the mid-19th century and are studied, primarily in relation to lakes and rivers, since the 1920`s (Erisman and Draaijers, 1995). Acidification has been perceived as a major environmental issue since the last 25 to 30 years. Acidification of soils and freshwaters in regions isolated from major sources of pollutants may have been enhanced due to the increased spreading of acidic pollutants caused by changes in fuel usage and combustion technology, (Lee, 1998). Direct deposition of pollutants usually, through runoff and in soil via flow from the surrounding results in the acidification of surface waters. Climate, shallow soils, and rapid flushing rate make higher altitudes more vulnerable to atmospheric inputs as compared to the lowlands (Mosello et al., 1995).

Complications related to acidification including effects on surface water, plants, vegetation and infrastructure are evident. Acidification of groundwater influences the geochemical equilibrium in soils and aquifers (Hansen and Postma 1995; Kjoller et al. 2004; Appleyard and Cook 2008). Elements such as Al, Mn, and other toxic metals become mobile due to acidic groundwaters making the waters unfit for drinking (Kjoller et al. 2004; Fest et al. 2005). Seasonal inequalities in acidity and the magnitude of acidification are generally inferior in groundwater than in surface water (Landers et al., 1994). As a fundamental part of the freshwater ecosystem, groundwater also contributes to the acidification of rivers and lakes through direct discharge. However, a major difficulty while studying spatio-temporal changes in groundwater acidification is soil heterogeneity. Knowledge of surface flow path distribution is complex and known to affect the residence time of infiltration of water in different soil horizons. Impacts of atmospheric deposition on surface water chemistry has been widely studied (e.g., Drablos and Tollan, 1980; N. van Breemen et al., 1983). However, the extent to which landscape changes interact with the effects of atmospheric deposition, either by exacerbating or counteracting surface water acidification, and has been investigated much less intensely. Landscape processes affect the acid-base chemistry of lakes and streams in a variety of ways by increasing or decreasing the concentrations of various ions in drainage waters. It is important to understand the quantitative importance of these processes in order to effectively manage water resources. Some processes contribute base cations to, or remove acid anions from, drainage waters thereby causing decreased acidity or surface water alkalization. Other processes remove base cations or contribute acid anions to solution, thereby causing acidification (N. van Breemen et al., 1983). Many of these landscape processes are influenced by natural and anthropogenic disturbances such as logging, fire, forest blow down, insect damage, road building, sewage discharge, wetlands drainage, and forest regrowth. The potential effects of landscape change on surface water acid-base chemistry were recently reviewed by Sullivan et al. (1996). Studies have also documented the acidity of groundwaters from the study area; however, very little is known about the degree and the level of acidification and more prominently the source and the rate of acidification. Inadequate management of soil and groundwater acidification in the study area can create instant and considerable long-term impacts with health, and environmental consequences such as:

1. Polluting water supplies with heavy metals and possibly triggering health issues if untreated water is used for drinking.
2. An added environmental consequence leading to corrosion and acidification of streams and other surface water bodies.

The study therefore seeks to use hydro-geochemical data to gain an preliminary understanding of groundwater acidity, identification of possible sources of acidity and its consequences for groundwater quality and its use in the study area.

Pune Metropolitan Region:

Drainage and geomorphology:

The Pune Metropolitan Region (PMR) is located at a distance of 150 kms south east of Mumbai in western India (Figure 1). Situated at a height of 560 m above the mean sea level the PMR is placed geographically near the western margin of the Deccan plateau amidst the hill ranges of Western Ghats mountain range paralleling the west coast India. The

region can be geomorphologically divided into hilly area, plateau and plains (Figure 2). The hills are the offshoots of the Western Ghats. To the west of the region, there are several highly dissected hill ranges. The Sinhagad hills to the south of the area are an important east-west water divide between the Mula-Mutha and Nira River basins. Extensive plateaus are developed in the study region. To the west and southwest there are large flat topped, but highly dissected plateaus. These are intensely fractured by N-S trending lineaments. A narrow discontinuous plateau is also developed on the Sinhagad hill ranges. Moderately dissected plateaus have developed at lower elevations especially in the north-western parts of the study area along the lower reaches of the Mutha River. Similarly, a large area of moderately dissected plateau is also present to the south of the study at the foot hills of the Sinhagad hill ranges. Moderately dissected plateaus have also developed to the north of the Mula-Mutha River. Ordinary dissected plateau surfaces have been developed along the Mula, Mutha, Pavana and Mula-Mutha Rivers. The plains in the study area are restricted to the lower reaches of the Mula-Mutha Rivers. They are generally represented by flat alluvial tracts.

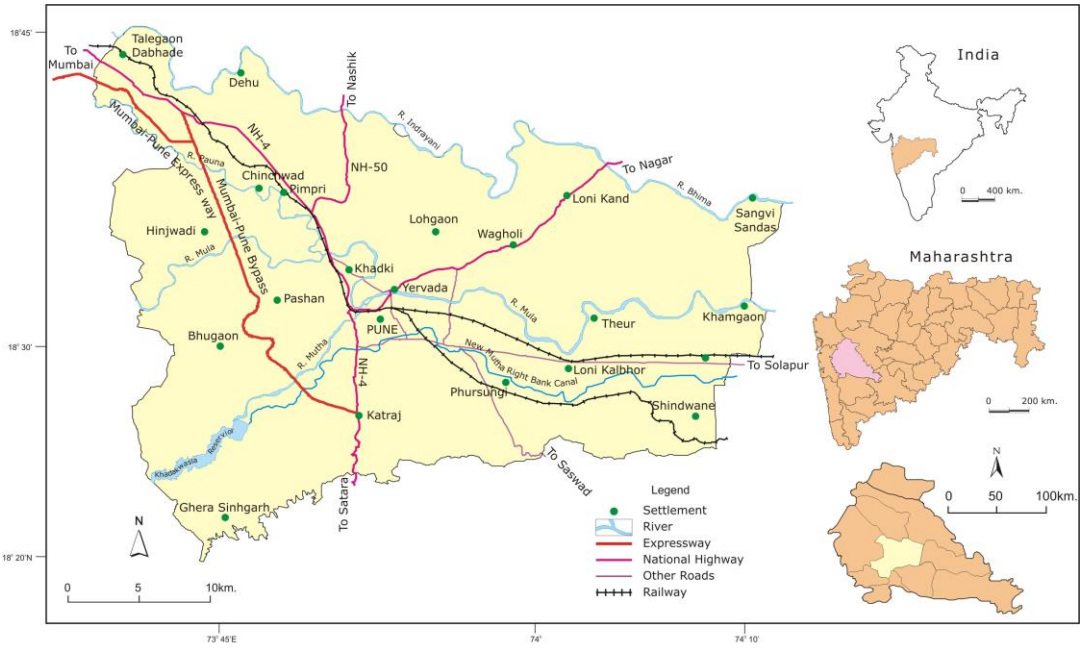

Figure 1: Location map of the study area

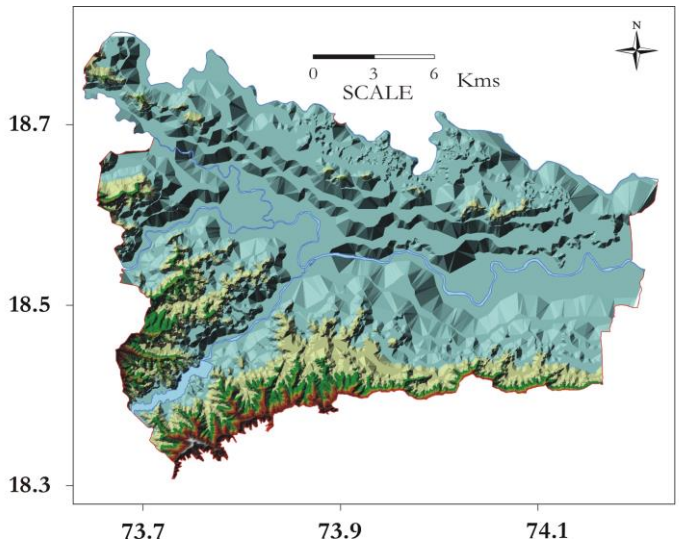

Figure 2: Geomorphology of the study area.

PMR is drained by Mula, Mutha, Pavana and Indrayani rivers. Pune city (Pune Municipal Corporation (PMC)) is situated near the confluence of Mula and Mutha rivers. Pavana and Indrayani are two more rivers traversing through the western outskirts of the urban area of PMR, administratively governed by separate Pimpri - Chinchwad Municipal Corporation (PCMC), an industrial township (Figure 1). On a regional scale all the above rivers drain into Bhima, which is a major tributary of Krishna River of peninsular India. All these rivers have their source areas in Western Ghats and mainly flow towards west. The PMC and PCMC urban areas extend over the gently sloping and undulating rocky areas forming the interfluves between the above rivers. Predominantly the industrial wastes pollute Pavana river, Mutha by domestic effluents and Mula and Indrayani by agricultural sources. Close to the major rivers the altitude drops below 560 m a.m.s.l. There are a few isolated and residual hills on the Indrayani-Pauna interfluves, where the elevation rises to 700 to 800 m above M.S.L The divide between Pavna and Mula is feature-less and rocky with outcrops of porphyritic basaltic flows, Chatushringi and Vetal hill ranges (800 m) lie inbetween Mula and Mutha. Soil cover is generally thin over most of the interfluves.

Geology of PMR:

Geologically, PMR is underlain mainly by Deccan Basalts of Cretaceous- Eocene age. The geology of the study area is characterized by simple as well as compound lava flows (Figure 3). The compound flows are restricted to the lower elevations whereas the simple flows to the elevation of above 680 m. The compound flows are vesicular and amygdaloidal at the top, whereas the middle sections are hard and compact in nature. They exhibit fracturing and jointing and are moderately weathered at places. The thickness of each flow is on an average above 20 meters and their basal sections are characterized by pipe amygdales. The vesicles are packed with zeolites, secondary silica, glass, green earth etc. The middle section of the flow consists of dark grey to black dense basalt.

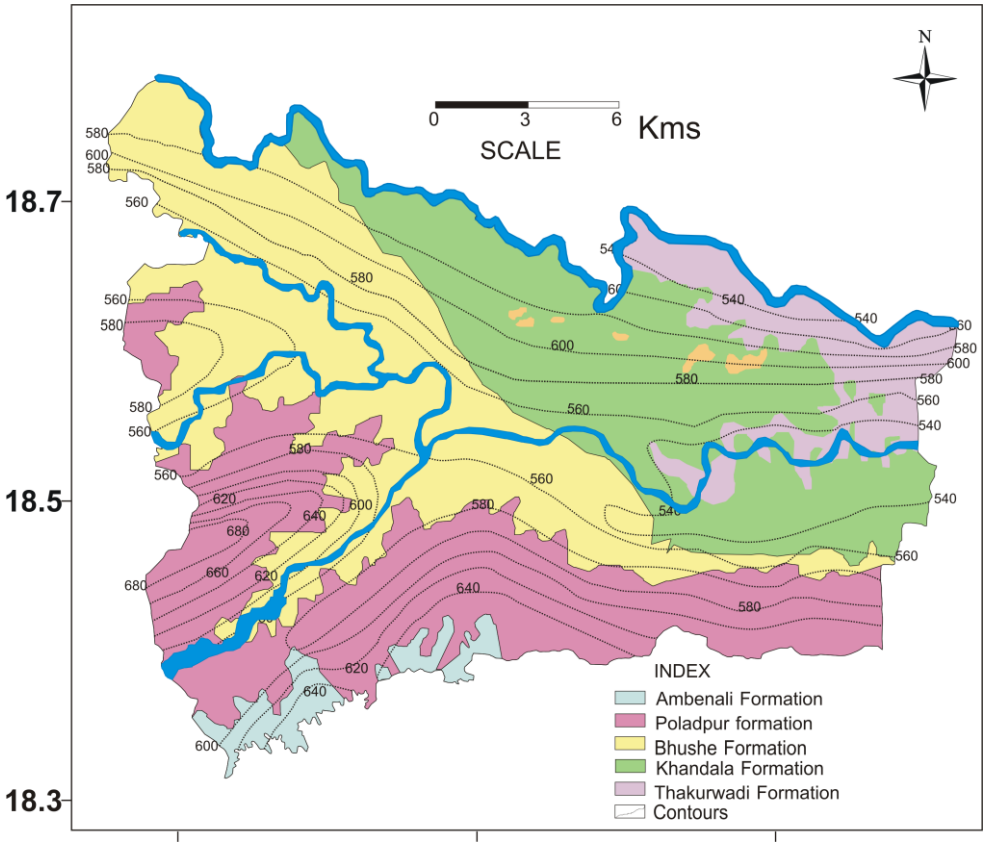

Figure 3: Geology of the study area.

A flows emerge amidst the pahoehoe flows in the riverbed of the Mula- Mutha River near Manjri. In the eastern part of the study area on the Pune-Ahmednagar Road and Pune - Solapur Road only pahoehoe flows are encountered. Pahoehoe flows are traced up to 724 m above M.S.L south of Pune city. Aa flows dominate the higher elevations. A total 20 Aa type flows with thickness varying from 7 to 42 m have been recorded on the Sinhgad hills in the southwest part of the study area. They occur at an altitude of 749 m to 1310 meters above mean sea level. Dykes are known to cut across these lava flows at various places essentially trending NNE-SSW, N-S and NNW-SSE.

The lava flows are separated by red bole horizons characterized by ferruginous clays of varying thickness (<1m to 1.5 m) and useful as marker horizons for flow separation. Many of these zones are referred as "bole beds" in Deccan Traps and they occur as prominent horizons showing red to brown, green, purple or grey colours, composed of fine-grained clayey material. Red bole horizons are seen outcropping near the Chaturshringi hills within the Pune city at an elevation of 595 m, in the southern part of the area along Pune-Saswad road in the Diveghat and in Katraj Ghat sections along Satara road.

Extensive geochemical studies of more than 3000m thick basalt pile from the Western Ghats have established detailed stratigraphic framework that includes three subgroups and twelve formations (Cox and Hawkesworth, 1985, Beane et al 1986, Subbarao et al 1994). Of these, the study area encompasses only five formations from top to bottom, which are Ambenali Formation (AF), Poladpur Formation (PF), Bhushe Formation (BF), Khandala Formation (KF) and Thakurwadi Formation (TF) (Figure 3)

The AF is composed of simple basalt flows and is a 400-meter-thick sequence as described by Cox and Hawkesworth (1985) resting over the PF and is capped by the Mahabaleshwar Formation (MF) exposed only in the Sinhagad Fort section. Average CaO / MgO ratio calculated from 2 representative basalt samples is 1.64, where as the Na_2O/ CaO ratio is 0.30. It characteristically has low LIL element concentrations, moderate to large HFS element abundances, and subsequently very small LIL/ HSF ratios. Low Ba, Rb, K_2O, ^{87}Sr / ^{86}Sr (Mahoney et al, 1982) is characteristic of this formation. The formation comprises of compact, massive plagioclase phyric basalt with mafic micro phenocrysts (Khadri et al, 1999).

PF is geochemically characterized by higher K_2O, Ba, Sr and lower Mg number (Beane et al, 1986). These rocks are fine to medium grained basalts typically carrying small phenocrysts of plagioclase + augite, or plagioclase+ augite+ olivine. Average of CaO/ MgO and Na_2O/ CaO ratios calculated from three representative samples from PF is 1.85 and 0.31 respectively.

BF is comprised of coarse grained, altered and amygdaloidal, aphyric or sparsely plagioclase phyric, compound lava flows. These flows are simple, commonly depicting oxidized tops. They are fine to medium grained basalts with small phenocrysts of plagioclase, augite and olivine (Beane et al, 1986). The formation is characterized by Karla Caves picrite basalt with MgO content as high as 12% and Ni > 280 ppm besides > 400 ppm Cr. It contains abundant olivine (Fo75 – Fo80) and clinopyroxene phenocrysts as well as large plagioclase glomero-porphyritic clusters. In this formation average values of CaO/ MgO and Na_2O/ CaO are 1.46 and 0.25 respectively. Thin section study revealed that the groundmass is deficient in opaque minerals, sparse plagioclase phenocrysts and micro phenocrysts and altered olivine are of very small size. In the eastern part of the area near Lonikand the Bushe Formation pinches out.

Khadri et al, (1999) have pointed out that in the south-eastern part of the PMR area, KF directly overlies the PF of Wai sub group. Presence of compact, massive, porphyritic basalt is the characteristic of this formation. Khandala Formation comprises essentially of simple flows generally columnar jointed characterized by geochemical constituents, which are higher in concentration of Al_2O_3, less in concentration of (TiO_2 1.2%-1.7%) and moderate MgO (6%) and low FeO (Beane. et al, 1986). As many as nine samples were studied to calculate the CaO/ MgO and Na_2O/ CaO ratios, where the average values generated were 1.56 and 0.30 respectively.

Thakurwadi Formation is composed of compound type of basalt flows with picritic horizons as well as more evolved flows. Chemical composition is relatively restricted with MgO = 7- 8% and TiO_2 in the range of 1.8-2 % (Beane. et al, 1986). This formation consists of thick sequence of coarse grained amygdaloidal, aphyric compound flows with well developed lava toes and appears to be highly altered. The CaO/MgO and Na_2O/ CaO ratios generated by averaging values of six samples were 1.41 and 0.25 respectively.

Rivers from the study area show presence of recent alluvial deposits as narrow belts all along. Thickness of these alluvium deposits varies between 5 to 15 metres and constitute less than one percent of the area. Lateral extent of the alluvium deposits ranges between 200 and 2000 m. The shallow alluvium deposits include loose or semi-consolidated medium to coarse grained sands, gravels, fine silt with admixture of clays lying directly on the massive, weathered or amygdaloidal zones of the basaltic lava flows.

Land use and land cover characteristics:

Character of the interaction between people and environment, and the influence of distance and resource base upon basic economic activities is reflected by the land use patterns. The term therefore, describes the function or use of an area of land put to man's activities (Clawson and Stewart 1965). Land cover mentions the "natural vegetation, water bodies and rock/soil, artificial cover and other features resulting due to land transformation". Urban expansion is a world phenomenon and PMR is no exception to this. Growing urbanisation of PMR is creating an alarming situation and has led to serious issues related to the land use such as loss of agricultural land, unauthorized urban sprawl, high land values, assumptions in land and other related problems. Rapid industrialization since 1960 in the region has led to a considerable change in the environment with respect to air, water and soil resources. Diversified modern manufacturing sector grew in and around the Pune city coupled with steady escalation of population in the area. The population of PMR according to the 1961 census was 9.93 lacs i.e. 40.3% of the Pune district population of which about 81% was urban (Shetye, 2000). The population increased to 29.71 lacs as per 1991 census followed by 44.85 lacs in 2001 and is expected to be close to 56 lacs by 2011. The PMR has grown at a disquieting rate due to rapid industrialization and urbanization with annual growth rates ranging from 3.5 to 1200% percent per annum over the last four decades in Pune city and Pune-Chinchwad Township respectively. Enlargement in the geographical spread and an astonishing swell in the population have enormously increased the pressure on the already limited land resources leading to a rapid change in land use pattern. Urban activities spilled beyond the former Pune city limits during the 1970's leading to the comprehensive and integrated planning of metropolitan region converging Pune be defined. Accordingly, Pune Metropolitan Region was established in July, 1967. Pune urban area or cluster as recognised by Central Government incorporates the areas under Pune and Pimpri- Chinchwad corporations besides Pune, Khadki and Dehu Road Cantonments and a few semi-urbanized villages on its periphery. Total area of PMR is 1544 sq. km. The Indian Remote Sensing Satellite (IRS) data was used to determine the present land use/land cover pattern of the PMR. In addition, topographical maps of the study area were used to generate the base map in order to understand the broad nature of land use before the advent of remote sensing techniques.

Various types of land use and land cover features like natural and stressed vegetation, cultivated area, barren and wasteland, and water bodies characterize the study area (Fig.4). Proportion of the area under vegetation cover and cultivation is significantly less. It is mostly dominated by barren and wasteland, followed by built-up and urban area. As per the GIS analysis it is evident that the urban and built-up areas are confined to the interfluves area, or concentrated along the Mumbai-Pune Pune-Banglore, Pune-Solpaur and Pune-Ahmednagar and the railway lines (Pawar et al 2001). Cultivated areas are restricted to the narrow valley-bottoms close to the Indrayani, Pauna and Mula Rivers and their tributaries. Barren area and wasteland are found to exist along the divide line between Indrayani and Pauna Rivers. Field observations reveal that this area is rocky and possess a thin soil wrap and miniature ephemeral streams.

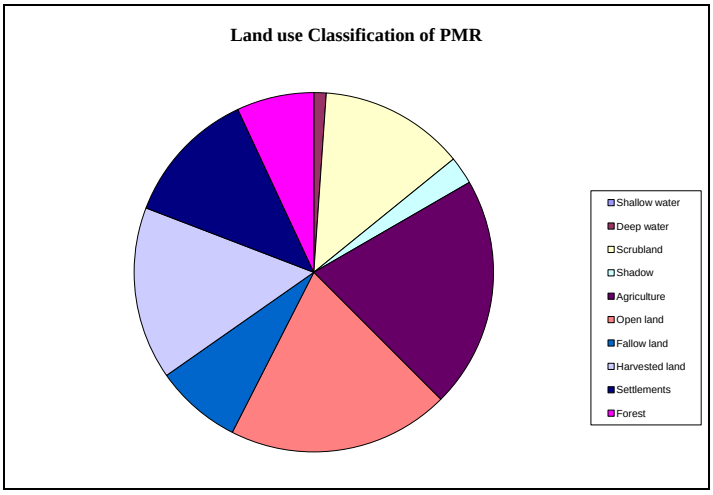

Figure 4: Pie chart showing land use classification of PMR

It is evident from the remote sensing analysis that the built-up and urban areas have recorded a historic raise and is mostly restricted to barren and wasteland area between the Mula- Mutha, Mula- Pavna and Indrayani- Pavna Rivers forming the highest part of the terrain. All the waste generated by urban and industrial areas is consequently, transported to the low-lying parts and ultimately to the streams and rivers. As a result, not only the surface waters but the groundwaters are also severely affected. In addition to these problems surface and groundwater, acidification poses a serious threat to human health as the local population is dependent on these water resources. In view of the fact that PMR is characterized by multiple land uses, the sources of pollution of groundwater are expected to be of diverse type. Such a complex situation demands need of an intricate remediation strategy. Consumption of inferior quality of water has posed risks to human health chiefly, in urban fringe areas that are more dependent on groundwater as their primary source of water. Therefore, the author endeavours to document the acidification of groundwater from PMR, which is a function of anthropogenic activity, topography and land use factors.

METHODOLOGY

Sample collection:

Due to variation of both hydrogeological, geological, land use and other environmental conditions in the study area, the sampling locations and sampling were designed to represent maximun factors as possible. Before sampling variety of environmental determinants such as type of land use, aquifer type and slope besides operating conditions of well were considered. In order to monitor fluctuations in the geochemistry of groundwater from PMR, four hydro-chemical surveys were conducted covering two pre-monsoon and two post-monsoon seasons during the period 2003 - 2005. In all 64 X 4 = 256 samples were collected and analyzed. The authors adopted a random grid method of sampling wherein 64 samples are approximately spaced out over a 4 sq km grid covering the entire 1544 sq km study area (Figure 5). In most of the hilly areas there were no wells available and hence it was not possible to get samples from such areas. These surveys permitted the author to get an perception into response of basaltic lithology to chemical weathering under characteristic monsoonal climatic setup. Main focus of the study being acquiring reliable information on the pollutants of the groundwater from the Pune Metropolitan region, and the controls over their dispersion and distribution patterns, the sampling stations falling under three main categories, viz dug wells, bore wells and surface water samples were considered. In all 19 dug wells, 43 bore wells and two surface water samples from rivers were chosen to represent the entire area.

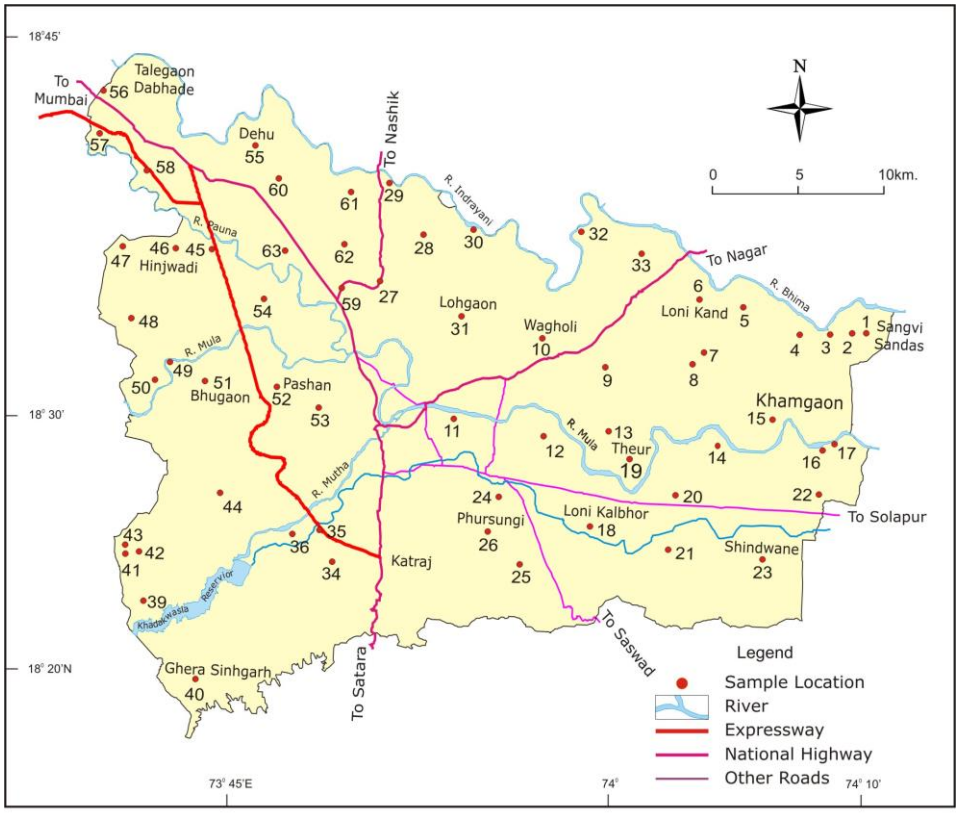

Figure 5: Ground water sampling locations

Analyses of water samples:
Water samples were analyzed for the determination of important chemical characteristics by using facilities in the Department of Geology, University of Pune. The pH and EC were determined in the field with the help of hand-held instruments. Major ionic constituents present in the groundwater were estimated using Dionex-600, High Performance Ion Chromatography System (HPIC) and Atomic Absorption Spectrophotometer. Anions were detected using AS-11-HC, 4mm column and potassium hydroxide as eluent 'A' and 12-milimolar, sodium hydroxide as eluent 'B'. Analytical conditions were set to a flow rate = 1.0 ml/min, injection volume 10 ml, temperature 30°C, with suppressed conductivity range 200 µS and ASRS-ULTRA auto suppression external water mode. Cations (Na, K, Mg and Ca) were analyzed using CS-12A analytical column. 25 ml sample was injected and 20 mM Methane Sulphonic Acid (MSA) was used as an eluent, a flow rate of 1.0 ml/min was maintained to pass the sample through cation self-regenerating suppressor (CSRS-ULTRA) at room temperature. Using this method, concentrations of F, Cl, NO_3, PO_4, SO_4, Na, K, Mg and Ca, were determined. Silica (SiO_2) concentrations were measured calorimetrically. Varian Spectra AA-220 AAS was used for the analyses of a few cationic and trace constituents. Resulting cation- anion charge balance errors are found to be within 10%, where majority samples fall within <5%.

Cationic evidences for acidification of groundwater from PMR. (Na, K, Ca and Mg):
Order of abundance of cations in the groundwater from PMR is Na>Ca>Mg>K and it remains the same for both seasons. Values of cations increase in the post-monsoon indicating enhanced rock-water interaction and mixing of waste waters in the native groundwater. Though the average concentrations of cations are comparable over the seasons, the spot specific minimum and maximum are variable indicating location specific dilution or concentration due to rainwater recharge or addition from polluted

sources in the vadose zone. On spatial scale, increase in Na from west to east can be attributed to hydro-geomorphological conditions (e.g. slope) and groundwater flow path, besides post-dissolution changes in the composition of water (Pawar et 2008). In comparison with other cations the K values are very low and do not show significant variations. A smaller amount of K concentration is mainly due to the non-appearance of K-bearing minerals (Subbarao et al 1994) excluding a few samples. Increase in K for S. No. NS1, WB8, TH19, DI27, LO31 and CI60 is a characteristic of fertilizers and mixing of domestic effluents. Mg concentrations depict slight increase in min. and max. values in post-monsoon, however the average values in post –monsoon has lowered as compared to pre-monsoon (Table 1 and 2). Elevated Mg values express a strong lithological control (Figure 6) due to the picritic horizons (MgO 5.0 to 12.03%) present in Bushe Formation (Beane, et al. 1986). Haul up in min. max. and avg. values of Ca in pre-monsoon indicate contribution from alluvium jacketed basaltic flows and secondary carbonates due to higher residence time (Figure 7). In the source areas of rivers, where alluvium is not in attendance, relatively lower values of Ca area recorded (Well. No. DG-6, KS-9, AP-15, UK-22, UD-26, TU-32, GS-40, MA-48 and DG-59). Isolated elevated Ca values are triggered by moderately superior interaction of groundwater with GPB flow, as also in the areas of low hydraulic gradient.

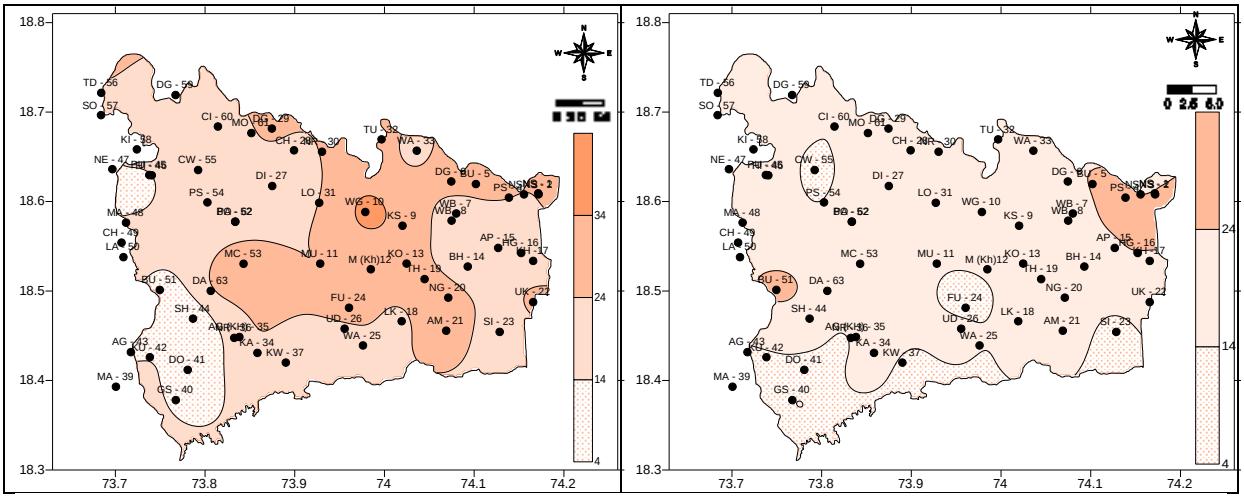

Figure 6: Spatio –temporal variations in average Mg concentrations in groundwaters from PMR

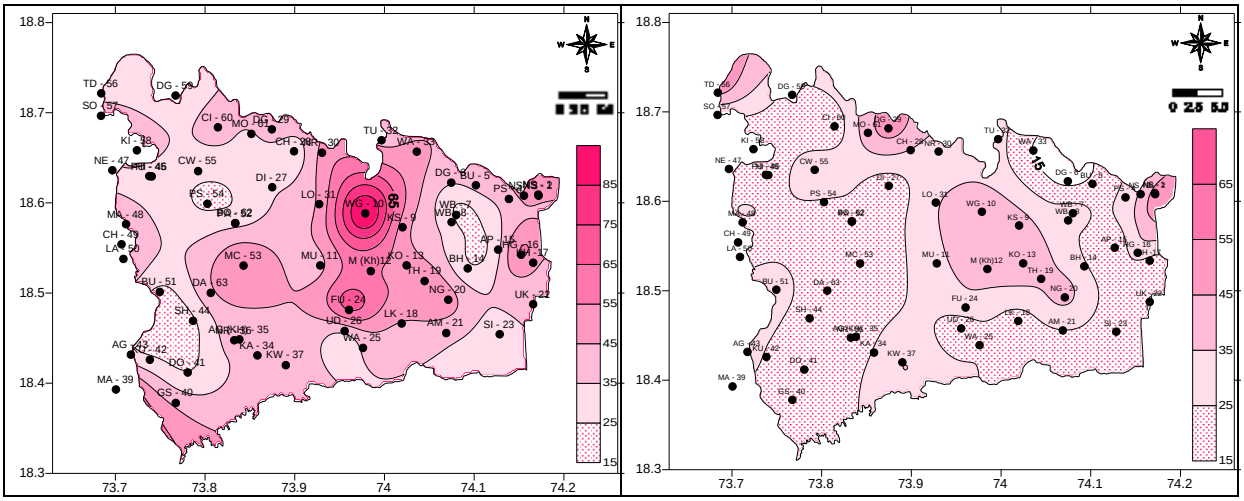

Figure 7: Spatio –temporal variations in average Ca concentrations of groundwaters from PMR

While, average Ca+Mg values (in equivalent units) are about 58.42% (range 54.72 – 62.12%) of the total cations, the Ca+Na account for 68.78% (68.78 – 69.26) representing major supply from weathering of mafic (olivine and pyroxene) and felsic (plagioclase feldspar) minerals in the basalts. Thus, signatures of chemical and mineralogical composition of associated basaltic rocks are represented in major cationic constituents of groundwater from the PMR area. Temporal divergence, exhibiting lesser average concentrations in pre- monsoon (except Na) and greater in post-monsoon (Table 1 and 2) can be explained by the cation concentrations. This is probably because of improved rainwater recharge due to enlarged surface area and enhanced rock-water interaction in post-monsoon. Difference of Ca records in pre and post monsoon seasons validates precipitation of carbonates. Hilly areas from picritic horizons in upland region of Bhushe Formation signify high Mg groundwater in post monsoon. As the recharge terminates in pre-monsoon the values decrease possibly due to absence of picritic horizons in low lying plains. High values of Mg indicate profusion of olivine + pyroxene in the host rock as its source (Rabemanana et al 2005). The Na shows inconsequential seasonal distinction in average values because of its conservative behaviour, though standard deviation in min. and max. values is higher in post monsoon could be possibly due to input from point sources of pollution. In nutshell, higher concentrations of Ca+Mg+Na in the groundwater during post-monsoon indicated increase in the volume of water in the aquifers thereby affecting solution of minerals and the ionic load.

Table 1: Average pre- monsoon physico-chemical analysis of groundwaters from PMR

Location	pH	Ec	TDS	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3
				epm	epm	epm	epm	epm			
NS - 1	7.58	2019.00	515.50	2.13	0.17	2.75	2.01	1.13	3.20	3.01	0.02
NS - 2	7.55	1453.00	430.30	2.20	0.06	1.91	2.11	0.85	2.38	2.64	0.19
NS - 3	7.81	317.00	337.55	2.47	0.08	2.47	1.87	0.42	2.05	1.32	0.03
PS - 4	7.98	1272.00	524.45	2.92	0.09	1.95	2.03	0.59	4.43	1.90	0.13
BU - 5	7.60	822.00	502.80	2.77	0.06	2.05	2.81	0.48	4.47	1.23	0.21
DG - 6	8.01	894.00	492.60	2.56	0.05	1.75	2.90	0.48	4.63	0.94	0.28
WB - 7	8.00	970.00	187.10	2.50	0.16	0.58	0.55	0.63	0.48	0.86	0.20
WB - 8	8.14	569.00	377.15	1.39	0.38	1.68	1.61	0.39	3.73	0.58	0.13
KS - 9	8.08	1334.00	623.35	4.20	0.14	2.26	2.66	0.74	5.41	0.94	0.69
WG - 10	7.47	1399.00	591.55	2.89	0.14	5.58	3.18	0.88	4.18	1.25	0.38
MU - 11	7.59	877.00	452.80	1.78	0.06	1.83	1.92	0.51	4.66	0.62	0.29
M (Kh)12	7.47	984.00	492.25	2.05	0.09	2.65	2.28	0.52	4.67	0.76	0.35
KO - 13	7.42	946.00	516.20	2.18	0.09	2.46	2.26	0.49	5.29	0.70	0.22
BH - 14	7.30	898.00	309.35	1.76	0.02	1.06	1.06	0.45	2.79	0.66	0.27
AP - 15	7.78	1359.00	629.55	4.67	0.06	1.25	1.35	0.55	6.48	0.97	0.29
HG - 16	7.28	1366.00	561.00	1.95	0.06	3.79	2.11	0.73	5.12	1.06	0.38
KH -17	7.53	1163.00	563.25	3.85	0.04	2.04	1.53	0.48	5.12	1.47	0.23
LK - 18	7.90	432.00	346.55	1.36	0.02	2.11	1.67	0.24	3.36	0.40	0.31
TH - 19	7.54	1439.00	619.55	3.37	0.23	2.80	2.30	0.69	5.37	1.23	0.62
NG - 20	7.49	1640.00	622.20	2.86	0.02	2.76	2.75	1.28	3.32	2.21	1.83
AM - 21	7.39	877.00	519.55	2.52	0.08	1.86	2.75	0.58	4.71	0.95	0.55
UK - 22	7.60	1021.00	521.85	2.21	0.06	2.11	2.32	0.79	5.04	0.72	0.46
SI - 23	7.90	436.00	296.40	1.34	0.04	1.40	1.19	0.38	2.87	0.51	0.14
FU - 24	7.14	1548.00	807.75	4.50	0.10	4.19	2.61	1.25	6.93	1.87	0.46
WA - 25	7.64	1030.00	583.85	3.13	0.06	1.87	1.86	0.76	5.33	0.87	0.91
UD - 26	7.94	885.00	418.40	2.34	0.19	1.12	1.66	0.62	4.06	0.56	0.29
DI - 27	7.83	600.00	441.60	2.43	0.41	1.78	1.33	0.50	4.26	0.55	0.23
CH - 28	7.24	1325.00	590.10	3.17	0.05	2.36	2.97	1.13	4.93	1.16	0.57

DG - 29	7.49	1009.00	524.00	2.09	0.03	2.58	2.20	0.82	4.34	0.99	0.89
NR - 30	7.54	709.00	458.95	1.97	0.03	2.15	1.99	0.59	4.26	0.77	0.45
LO - 31	7.42	1368.00	597.55	3.27	0.64	1.92	2.40	1.10	4.51	1.31	0.86
TU - 32	7.67	772.00	437.70	2.06	0.13	2.40	1.47	0.53	3.73	0.93	0.46
WA - 33	7.69	769.00	519.80	3.02	0.09	1.87	2.03	0.47	5.29	0.63	0.25
KA - 34	7.44	729.00	420.00	2.23	0.05	1.64	1.76	0.54	4.14	0.56	0.24
AG (BK) - 35	7.46	518.00	405.20	2.16	0.04	2.15	1.37	0.30	4.34	0.22	0.13
NR - 36	7.50	779.00	418.80	2.17	0.03	2.32	1.42	0.51	3.98	0.42	0.38
MA - 39	7.27	524.00	365.70	2.79	0.10	1.09	0.73	0.47	3.61	0.57	0.05
GS - 40	7.34	392.00	256.80	1.03	0.02	1.34	1.31	0.33	2.66	0.27	0.05
DO - 41	7.46	576.00	371.20	2.36	0.04	1.14	0.82	0.38	4.10	0.29	0.08
KU - 42	7.61	486.00	244.20	1.91	0.04	1.01	0.31	0.29	2.38	0.23	0.13
AG - 43	7.80	372.00	242.50	1.42	0.02	1.25	0.66	0.26	2.54	0.18	0.05
SH - 44	7.52	562.00	320.60	1.15	0.02	1.45	1.15	0.21	3.65	0.27	0.12
PU - 45	7.18	479.00	294.35	1.07	0.01	1.52	0.94	0.22	3.16	0.27	0.23
HI - 46	7.48	762.00	333.85	1.11	0.01	2.28	1.27	0.50	2.62	0.71	0.57
NE - 47	7.27	665.00	433.00	1.13	0.01	1.77	1.23	0.32	4.92	0.37	0.44
MA - 48	7.47	752.00	458.45	1.75	0.02	2.57	2.15	0.45	4.39	0.59	0.46
CH - 49	7.81	493.00	329.05	2.42	0.02	0.96	0.57	0.23	3.65	0.17	0.12
LA - 50	7.49	550.00	358.70	1.15	0.01	1.80	1.56	0.21	4.10	0.13	0.22
BU - 51	7.44	1103.00	614.70	1.95	0.22	2.93	2.53	0.50	6.76	0.51	0.29
PA - 52	7.77	465.00	334.30	1.84	0.04	1.03	1.46	0.17	3.77	0.21	0.10
MC - 53	6.99	634.00	435.00	1.89	0.03	1.36	2.15	0.31	5.12	0.26	0.02
PS - 54	7.74	595.00	365.70	1.64	0.02	1.62	2.01	0.35	3.93	0.28	0.08
CW - 55	7.67	546.00	358.35	2.30	0.04	1.94	1.12	0.32	3.65	0.30	0.06
TD - 56	7.55	671.00	381.95	2.03	0.05	2.39	1.98	0.33	3.65	0.29	0.22
SO - 57	7.41	392.00	296.10	1.09	0.02	1.15	1.71	0.10	3.52	0.10	0.06
KI - 58	7.25	708.00	396.55	1.98	0.03	2.18	1.33	0.37	4.14	0.31	0.16
DG - 59	7.57	512.00	364.45	1.56	0.16	1.51	1.65	0.27	3.98	0.26	0.13
CI - 60	7.63	468.00	327.50	1.01	0.66	1.27	1.58	0.28	3.40	0.24	0.08
MO - 61	7.51	892.00	472.40	1.79	0.14	2.31	2.17	0.47	4.75	0.59	0.30
BO - 62	7.14	587.00	338.70	1.74	0.05	1.20	1.84	0.28	3.36	0.54	0.16
DA - 63	7.46	605.00	412.45	1.86	0.04	1.21	1.87	0.31	4.84	0.29	0.02
AVG	7.53	756.00	438.74	2.20	0.10	1.96	1.78	0.51	4.11	0.75	0.30
MIN	6.99	317.00	187.10	1.01	0.01	0.58	0.31	0.10	0.48	0.10	0.02
MAX	8.14	2019.00	807.75	4.67	0.66	5.58	3.18	1.28	6.93	3.01	1.83
STD DEV	0.34	413.00	147.25	1.95	2.30	2.67	2.94	3.38	3.54	4.13	4.52

Table 2: Average post- monsoon physico-chemical analysis of waters from PMR

Location	**pH**	**Ec**	**TDS**	**Na**	**K**	**Ca**	**Mg**	**Cl**	**HCO_3**	**SO_4**	**NO_3**
				epm	epm	epm	epm	epm			
NS - 1	7.58	2019	515.5	2.13	0.17	2.75	2.01	1.13	3.2	3.01	0.02
NS - 2	7.55	1453	430.3	2.2	0.06	1.91	2.11	0.85	2.38	2.64	0.19
NS - 3	7.81	317	337.55	2.47	0.08	2.47	1.87	0.42	2.05	1.32	0.03
PS - 4	7.98	1272	524.45	2.92	0.09	1.95	2.03	0.59	4.43	1.9	0.13
BU - 5	7.6	822	502.8	2.77	0.06	2.05	2.81	0.48	4.47	1.23	0.21
DG - 6	8.01	894	492.6	2.56	0.05	1.75	2.9	0.48	4.63	0.94	0.28
WB - 7	8	970	187.1	2.5	0.16	0.58	0.55	0.63	0.48	0.86	0.2
WB - 8	8.14	569	377.15	1.39	0.38	1.68	1.61	0.39	3.73	0.58	0.13
KS - 9	8.08	1334	623.35	4.2	0.14	2.26	2.66	0.74	5.41	0.94	0.69
WG - 10	7.47	1399	591.55	2.89	0.14	5.58	3.18	0.88	4.18	1.25	0.38
MU - 11	7.59	877	452.8	1.78	0.06	1.83	1.92	0.51	4.66	0.62	0.29
M (Kh)12	7.47	984	492.25	2.05	0.09	2.65	2.28	0.52	4.67	0.76	0.35

KO - 13	7.42	946	516.2	2.18	0.09	2.46	2.26	0.49	5.29	0.7	0.22
BH - 14	7.3	898	309.35	1.76	0.02	1.06	1.06	0.45	2.79	0.66	0.27
AP - 15	7.78	1359	629.55	4.67	0.06	1.25	1.35	0.55	6.48	0.97	0.29
HG - 16	7.28	1366	561	1.95	0.06	3.79	2.11	0.73	5.12	1.06	0.38
KH -17	7.53	1163	563.25	3.85	0.04	2.04	1.53	0.48	5.12	1.47	0.23
LK - 18	7.9	432	346.55	1.36	0.02	2.11	1.67	0.24	3.36	0.4	0.31
TH - 19	7.54	1439	619.55	3.37	0.23	2.8	2.3	0.69	5.37	1.23	0.62
NG - 20	7.49	1640	622.2	2.86	0.02	2.76	2.75	1.28	3.32	2.21	1.83
AM - 21	7.39	877	519.55	2.52	0.08	1.86	2.75	0.58	4.71	0.95	0.55
UK - 22	7.6	1021	521.85	2.21	0.06	2.11	2.32	0.79	5.04	0.72	0.46
SI - 23	7.9	436	296.4	1.34	0.04	1.4	1.19	0.38	2.87	0.51	0.14
FU - 24	7.14	1548	807.75	4.5	0.1	4.19	2.61	1.25	6.93	1.87	0.46
WA - 25	7.64	1030	583.85	3.13	0.06	1.87	1.86	0.76	5.33	0.87	0.91
UD - 26	7.94	885	418.4	2.34	0.19	1.12	1.66	0.62	4.06	0.56	0.29
DI - 27	7.83	600	441.6	2.43	0.41	1.78	1.33	0.5	4.26	0.55	0.23
CH - 28	7.24	1325	590.1	3.17	0.05	2.36	2.97	1.13	4.93	1.16	0.57
DG - 29	7.49	1009	524	2.09	0.03	2.58	2.2	0.82	4.34	0.99	0.89
NR - 30	7.54	709	458.95	1.97	0.03	2.15	1.99	0.59	4.26	0.77	0.45
LO - 31	7.42	1368	597.55	3.27	0.64	1.92	2.4	1.1	4.51	1.31	0.86
TU - 32	7.67	772	437.7	2.06	0.13	2.4	1.47	0.53	3.73	0.93	0.46
WA - 33	7.69	769	519.8	3.02	0.09	1.87	2.03	0.47	5.29	0.63	0.25
KA - 34	7.44	729	420	2.23	0.05	1.64	1.76	0.54	4.14	0.56	0.24
AG (BK) - 35	7.46	518	405.2	2.16	0.04	2.15	1.37	0.3	4.34	0.22	0.13
NR - 36	7.5	779	418.8	2.17	0.03	2.32	1.42	0.51	3.98	0.42	0.38
MA - 39	7.27	524	365.7	2.79	0.1	1.09	0.73	0.47	3.61	0.57	0.05
GS - 40	7.34	392	256.8	1.03	0.02	1.34	1.31	0.33	2.66	0.27	0.05
DO - 41	7.46	576	371.2	2.36	0.04	1.14	0.82	0.38	4.1	0.29	0.08
KU - 42	7.61	486	244.2	1.91	0.04	1.01	0.31	0.29	2.38	0.23	0.13
AG - 43	7.8	372	242.5	1.42	0.02	1.25	0.66	0.26	2.54	0.18	0.05
SH - 44	7.52	562	320.6	1.15	0.02	1.45	1.15	0.21	3.65	0.27	0.12
PU - 45	7.18	479	294.35	1.07	0.01	1.52	0.94	0.22	3.16	0.27	0.23
HI - 46	7.48	762	333.85	1.11	0.01	2.28	1.27	0.5	2.62	0.71	0.57
NE - 47	7.27	665	433	1.13	0.01	1.77	1.23	0.32	4.92	0.37	0.44
MA - 48	7.47	752	458.45	1.75	0.02	2.57	2.15	0.45	4.39	0.59	0.46
CH - 49	7.81	493	329.05	2.42	0.02	0.96	0.57	0.23	3.65	0.17	0.12
LA - 50	7.49	550	358.7	1.15	0.01	1.8	1.56	0.21	4.1	0.13	0.22
BU - 51	7.44	1103	614.7	1.95	0.22	2.93	2.53	0.5	6.76	0.51	0.29
PA - 52	7.77	465	334.3	1.84	0.04	1.03	1.46	0.17	3.77	0.21	0.1
MC - 53	6.99	634	435	1.89	0.03	1.36	2.15	0.31	5.12	0.26	0.02
PS - 54	7.74	595	365.7	1.64	0.02	1.62	2.01	0.35	3.93	0.28	0.08
CW - 55	7.67	546	358.35	2.3	0.04	1.94	1.12	0.32	3.65	0.3	0.06
TD - 56	7.55	671	381.95	2.03	0.05	2.39	1.98	0.33	3.65	0.29	0.22
SO - 57	7.41	392	296.1	1.09	0.02	1.15	1.71	0.1	3.52	0.1	0.06
KI - 58	7.25	708	396.55	1.98	0.03	2.18	1.33	0.37	4.14	0.31	0.16
DG - 59	7.57	512	364.45	1.56	0.16	1.51	1.65	0.27	3.98	0.26	0.13
CI - 60	7.63	468	327.5	1.01	0.66	1.27	1.58	0.28	3.4	0.24	0.08
MO - 61	7.51	892	472.4	1.79	0.14	2.31	2.17	0.47	4.75	0.59	0.3
BO - 62	7.14	587	338.7	1.74	0.05	1.2	1.84	0.28	3.36	0.54	0.16
DA - 63	7.46	605	412.45	1.86	0.04	1.21	1.87	0.31	4.84	0.29	0.02
AVG	8.19	732.00	438.74	2.20	0.10	1.96	1.78	0.51	4.11	0.75	0.30
MIN	6.99	317.00	187.10	1.01	0.01	0.58	0.31	0.10	0.48	0.10	0.02
MAX	8.14	2019.00	807.75	4.67	0.66	5.58	3.18	1.28	6.93	3.01	1.83
STD DEV	0.34	413	147.25	1.95	2.3	2.67	2.94	3.38	3.54	4.13	4.52

Anionic evidences for acidification of groundwater from PMR. (HCO_3, Cl, SO_4, NO_3):

Influence of various geochemical and biochemical processes active in breaking down of rock minerals is reflected by the anions present in the groundwater from PMR (U.S.G.S., 1993). Comparison of anion data suggest that bicarbonate is the principal anion followed by SO_4> Cl>NO_3 suggesting weathering of silicates as the main source of ions in the groundwater accompanied by anthropogenic inputs. The HCO_3 accounts for more than 65% (range 65% in pre- and 85% in post-monsoon) of the total anions present in the groundwater (Table 1 and 2). Anion plots (Figure 8) depicts moderate seasonal discrepancy in bicarbonate. Increase in HCO_3 in pre- monsoon (avg. 252 ppm) entails 1] precipitation of mineral salts and loss of CO_2 2] continuous infiltration of urban wastewaters into the aquifers. This in turn has lead to acidification of groundwater evidenced by drop in pre-monsoon pH values by unit of 0.65 (Foppen, 2002) (Fig. 9). Increase in anthropogenic allies like SO_4+Cl in pre-monsoon corroborates this inference. On the other hand, enhanced rainwater recharge and accessibility of larger surface area for rock–water interaction in post monsoon is confirmed by enhanced pH and lowered HCO_3 values (Matthess and Harvey, 1982;). Vesicular severance of compound flows of Bhushe Formation being vulnerable to weathering, possibly promoted solution of rock minerals related to persistent recharge in this season. Higher proportion of HCO_3 to other anions, its origin related to weathering of primary silicate minerals dominated by alkaline earths and HCO_3>SO_4+Cl as indicator of rock weathering is strongly considered by Datta and Tyagi, (1996).

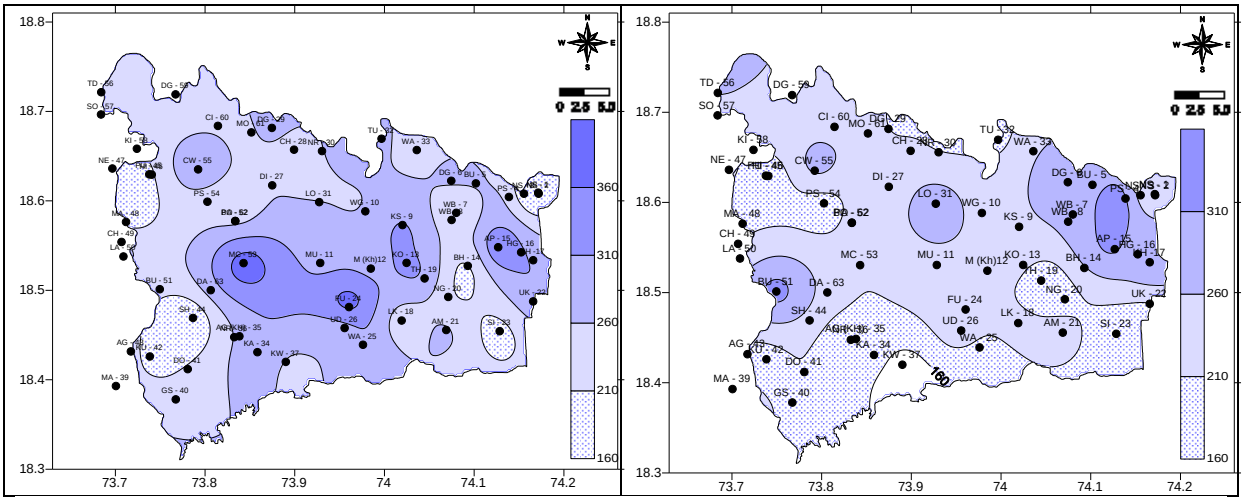

Figure 8: Spatio –temporal variations in average HCO_3 concentrations of groundwaters from PMR

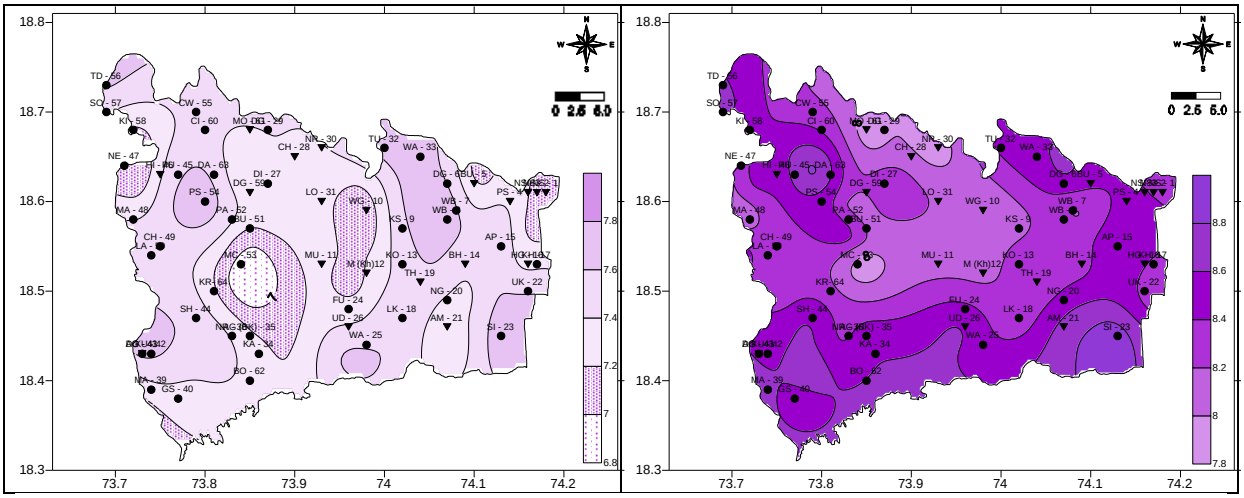

Figure 9: Spatio –temporal variations in average pH concentrations of groundwaters from PMR

Chloride in the groundwaters from the study area is not significant under conditions of weathering process as the basaltic lithology is lacks Cl-bearing minerals. Therefore, chloride in the groundwaters can be attributed to sea salts or human activities. Apart from bicarbonates, Cl, SO_4 and NO_3 are likely to be contributed via precipitation and by human activities. On spatial scale there is remarkable variation in Cl values (10 to 15 % of the total cations in post and pre-monsoon respectively), which is evidenced by high concentrations in urban and irrigated areas. The temporal disparity of Cl indicates negligible fluctuation with isolated raise from fertilizer/animal/ human waste sources (Pawar and Shaikh, 1995) (Figure 10). In conclusion, the possible origin of Cl in the area is attributed to 1] rainwater that has intensified due to evaporation in the shallow soil horizons and 2] wastewater charge from leaky sewers, lower-order unlined streams loaded with urban effluents and, use of fertilizers such as KCl in irrigated agriculture (Foppen, 2002). Since Cl contribution is from human activities, it is considered as an indicator of pollution in the present case (Hem, 1991). The rainwater Cl is not expected to exceed 40 mg/L as background in recharge, hence very high values unveil sources other than the rain (Pawar et al 2016).

Nitrate swings over from 4.54% of the total anions in post-monsoon to 16.7% in pre-monsoon. Elevated NO_3 values in pre-monsoon are possibly due to input from urban wastewater and agricultural sources. On the spatial scale high concentration NO_3 anomalies corresponding with urban and intensive agriculture areas (Figure 11) confirm urban effluents and nitrogen fertilizers (e.g. urea) as additional sources (Pawar and Shaikh, 1995, Pawar et al 2008. Pawar et al 2016). The scatter plots of NO_3 vs. Cl and Cl vs SO_4 depicted in Fig. 12 a and b show a significant positive correlation, thus authenticating their origin from a common source. While, Cl and NO_3 are accredited to the combined effect of fertilizers and rainfall (Pawar and Shaikh, 1995) the average sulphate values in the pre- and post-monsoon with moderate seasonal fluctuation (14.9% of the total anions in post-monsoon to 18.2% in pre-monsoon) suggest wastewaters and agricultural sources. This is confirmed by hoist in its concentration in urban and agricultural areas towards the east. In nutshell, the anthropogenic constituents have increased by about 3.3% in the case of SO_4, 11.11% in Cl, and 12.16% in NO_3 in pre-monsoon with a concomitant decrease in HCO_3 from 85% in post-monsoon to 65% in pre-monsoon. This increase in the anthropogenic components is responsible for decreasing the pH by unit of 0.65 leading to acidification of groundwater in the urban areas of PMR.

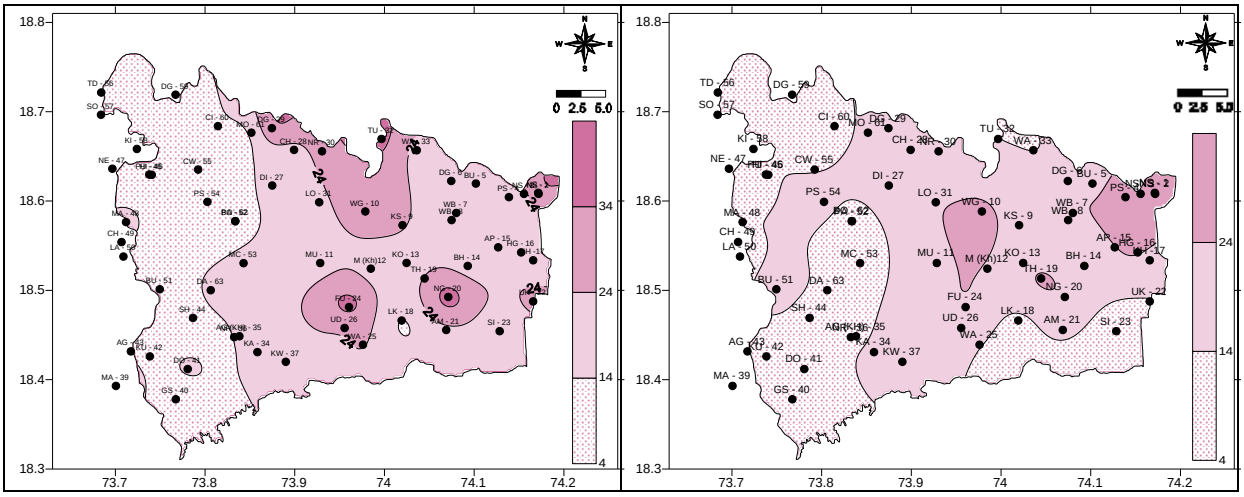

Figure 10: Spatio –temporal variations in average Cl concentrations of groundwaters from PMR

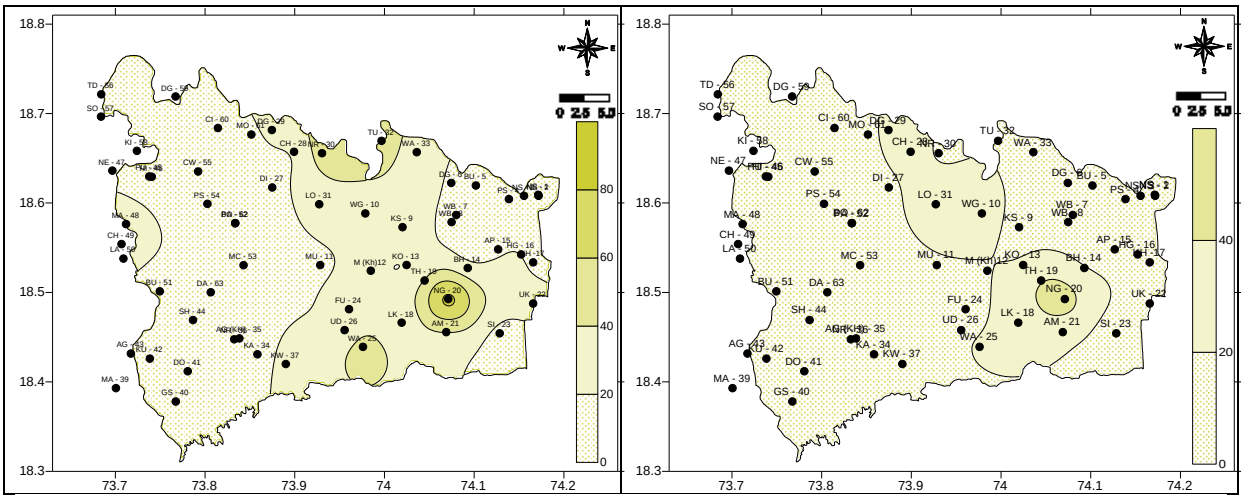

Figure 11: Spatio –temporal variations in average NO3 concentrations of groundwaters from PMR

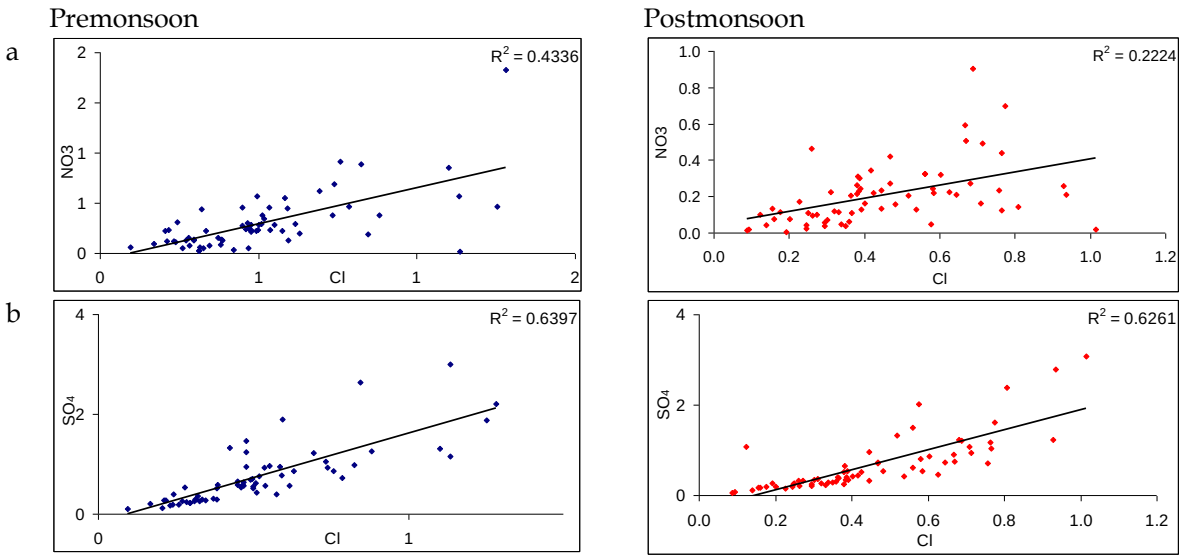

Figure 12 (a, b): Scatter plots of NO_3 vs. Cl and Cl vs. SO_4

Groundwater acidification in PMR:

Overall decrease in pH values (pre-monsoon avg. pH = 7.53, post-monsoon avg. pH = 8.19) and concomitant increase in EC (pre-monsoon avg. EC = 756 µS/cm, post-monsoon avg. EC = 732 µS/cm) in the PMR area suggests acidification of shallow groundwater aquifers. Acidification index values were therefore calculated by using expression (Kortatsi et al 2008): Aci = 0.93 (Ca+Mg) -14-alk) (Table 3). Negative values of Aci for all the wells in the study area thus revalidate acidification of shallow ground water aquifers (Figure 13). Likewise, the acid neutralising capacity of the groundwater was also computed using the formula (Stumm 1992): ANC = (Ca+Mg+Na+K – NO_3+SO_4+Cl). ANC values for the groundwater from PMR vary from avg. 4.47 in pre-monsoon to avg. 3.90 in post-monsoon. (Table 3). Positive values thus indicate that in spite of acidification, (Figure 14) the groundwater still has the potential to neutralise the acids possibly due to abundance of cation alumino-silicates dominating basaltic lithology that hosts the shallow aquifers.

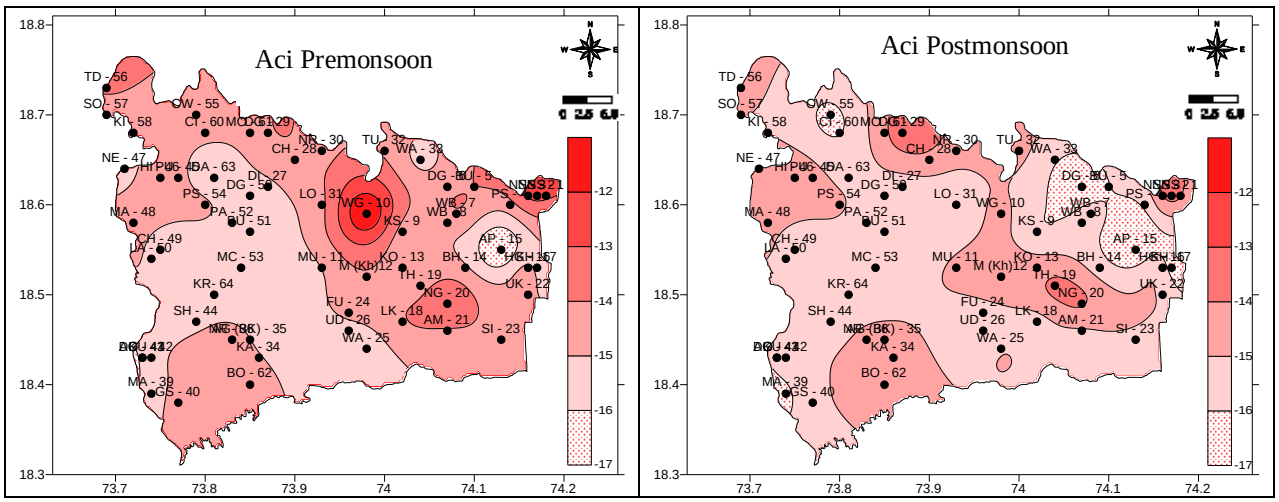

Figure 13: Isolines indicating Acidification of the study area

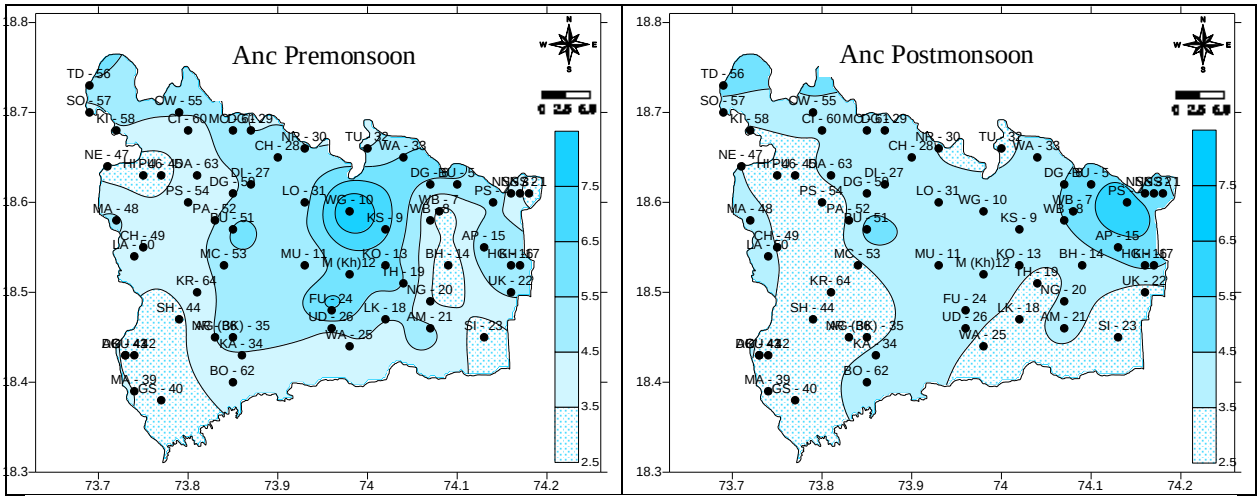

Figure 14: Isolines indicating Acid Neutralizing Capacity of the Study area

Table 3: ACI and ANC values of groundwaters from PMR

Sample No.	Premonsoon		Postmonsoon	
	Aci	ANC	Aci	ANC
NS - 1	-12.77	2.90	-14.44	4.39
NS - 2	-12.64	2.60	-11.75	6.53
NS - 3	-12.01	5.12	-13.86	3.48
PS - 4	-14.73	4.37	-16.26	7.28
BU - 5	-13.95	5.77	-16.02	5.05
DG - 6	-14.31	5.56	-16.94	4.52
WB - 7	-13.43	2.10	-15.29	4.77
WB - 8	-14.67	3.96	-15.78	4.45
KS - 9	-14.83	6.89	-16.20	4.39
WG - 10	-10.03	9.28	-14.48	3.93
MU - 11	-15.17	4.17	-14.71	4.02
M (Kh)12	-14.09	5.44	-14.22	4.26
KO - 13	-14.90	5.58	-14.46	4.47
BH - 14	-14.82	2.52	-15.64	3.88
AP - 15	-18.06	5.52	-17.54	4.86
HG - 16	-13.63	5.74	-14.30	5.04
KH -17	-15.80	5.28	-17.58	4.80
LK - 18	-13.84	4.21	-15.65	3.33
TH - 19	-14.63	6.16	-13.38	2.51
NG - 20	-12.20	3.07	-13.39	3.86
AM - 21	-14.42	5.13	-15.39	3.85
UK - 22	-14.92	4.73	-14.93	2.71
SI - 23	-14.46	2.94	-15.13	2.67
FU - 24	-14.61	7.82	-15.37	3.74
WA - 25	-15.86	4.38	-14.74	2.91
UD - 26	-15.47	3.84	-16.24	4.17
DI - 27	-15.37	4.67	-15.68	3.02
CH - 28	-13.97	5.69	-14.13	4.60
DG - 29	-13.89	4.20	-12.98	4.15
NR - 30	-14.41	4.33	-14.62	3.16
LO - 31	-14.49	4.96	-16.24	4.28
TU - 32	-14.13	4.14	-14.55	3.21
WA - 33	-15.66	5.66	-16.02	3.87
KA - 34	-14.98	4.34	-14.45	3.92
AG (BK) - 35	-15.07	5.07	-14.87	2.99
NR - 36	-14.50	4.63	-14.68	2.92
MA - 39	-15.92	3.62	-16.47	3.37
GS - 40	-14.20	3.05	-15.21	2.87
DO - 41	-16.28	3.61	-15.96	3.52
KU - 42	-15.15	2.62	-15.08	3.08
AG - 43	-14.76	2.86	-14.08	3.82
SH - 44	-15.23	3.17	-15.59	3.42
PU - 45	-14.87	2.82	-14.53	3.22
HI - 46	-13.32	2.89	-14.03	2.70
NE - 47	-16.13	3.01	-14.61	3.57
MA - 48	-14.00	4.99	-14.42	4.03
CH - 49	-16.23	3.45	-16.18	3.37
LA - 50	-14.98	3.96	-15.09	3.85
BU - 51	-15.68	6.33	-16.19	5.39

PA - 52	-15.45	3.89	-15.78	3.38
MC - 53	-15.86	4.84	-15.23	3.18
PS - 54	-14.55	4.58	-14.60	2.76
CW - 55	-14.80	4.72	-16.44	4.38
TD - 56	-13.59	5.61	-14.51	5.30
SO - 57	-14.86	3.71	-15.09	3.45
KI - 58	-14.88	4.68	-14.98	3.35
DG - 59	-15.04	4.22	-15.41	3.88
CI - 60	-14.75	3.92	-16.26	3.32
MO - 61	-14.58	5.05	-14.19	4.60
BO - 62	-14.53	3.85	-14.54	4.02
DA - 63	-15.98	4.36	-15.50	3.90
Avg	-14.63	4.47	-15.11	3.90
Mean	-18.06	2.10	-17.58	2.51
Max	-10.03	9.28	-11.75	7.28
Std Dev	1.18	1.32	1.05	0.90

According to Appelo and Postma (1999), pH of natural groundwater is unaffected by anthropogenic activities and is expected to be not less than 4.5. Therefore, the samples with reasonable acidity have little or no form of anthropogenic inputs of acidity. Natural processes such as the production of carbonic acid from atmospheric carbon dioxide during rainfall, or other natural processes like the dissolution of carbon dioxide generated from soil root respiration is associated with moderate acidity accompanied by lower EC (Knutsson 1994).

Low levels of nitrates in the water samples indicates absence of anthropogenic inputs. Samples from industrial/urban area which show an acidic character have high concentration of the major anions particularly nitrates reflecting the influence of anthropogenic inputs. Presence of multiple industries and high traffic density in the area suggests that acidic atmospheric deposition could be a source of anthropogenic input on the shallow groundwater quality and acidity.

SUMMARY AND CONCLUSIONS

Acidification is a serious threat to the groundwater quality in this province, causing both corrosion of water pipe systems and increased leaching of metals from the ground. The studies were undertaken on documenting the acidification of groundwater in the Pune Metropolitan Region of Western India which is one of the fastest rising industrial regions located at a distance of 140 km south of Mumbai. Therefore, studies were conducted in order to delineate the spatial and intra-annual trends in the geochemical characteristics of groundwater. The astounding increase in the population and bulging urban sprawl have enormously amplified the pressure on the already limited land and water resources in addition causing pollution of air, water and soil. The results were used in deriving a relationship between groundwater acidification with land use, topography and anthropogenic activities. Results however, indicated that groundwater chemistry is basically a function of composition of the basaltic lithology, followed by geomorphologic and land use characteristics.

In general, inputs of Cl, SO_4 and NO_3 were related to rainfall and land use factors such as industrialisation, urbanisation and irrigated agriculture. Positive correlations between Mg vs. HCO_3 and Ca+Mg vs. HCO_3 and Na+K vs. HCO_3 support dissolution of mafic and felsic minerals from the basaltic lithology. Similarly, the positive correlations between Cl vs. NO_3, Cl vs. SO_4 and well elevations vs. ionic concentrations respectively confirm role of land use variables and topography on groundwater chemistry.

The study thus puts forward the interpretation that acidification of groundwater in PMR is a function of land use, topography and anthropogenic activities. Decline in pH values and concomitant increase in EC in the areas under intense urbanization is suggestive of acidification of groundwater in PMR. The acidification index and acid neutralization capacity confirm this inference.

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