Physicochemical Characterization of Groundwater in Urban Areas of Lahore, Pakistan, with Special Reference to Arsenic

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Summary: The current quality status of groundwater from Lahore was investigated using standard analytical methodologies. The physicochemical parameters included in the study were pH, alkalinity, electrical conductivity, TDS, hardness, bicarbonate, nitrate, chloride, fluoride, sulphate, phosphate and turbidity. The metals included in the study were Na, K, Ca, Mg, Fe, Pb and As. The waters ranged in pH from 7.50 to 8.20 and in conductance from 329 to 1090 μS/cm. The alkalinity and TDS of the groundwater vary from 2.80 to 8.20 m.mol/L and 198 to 762 mg/L, respectively. Most of the water samples were found to be genuinely hard (100 to 300 mg/L hardness) and have rather low chloride and fluoride concentrations. The bicarbonate and nitrate ranged from 140 to 410 mg/L and 0.70 to 2.00 mg/L, respectively. The average metal concentrations followed the order; Na > Ca > Mg > K > Fe > As > Pb. For As, the concentration ranged from 24.6 to 71.6 μg/L, with the mean concentration of 36.0 μg/L, thus exceeding the upper permissible safe limit of As (10 μg/L) laid down by WHO and USEPA. The correlation study showed significant relationships among various physicochemical parameters and selected metal pairs. Multivariate cluster analysis was used for the apportionment of the measured variables and it revealed both natural and anthropogenic intrusion in the groundwater.

Introduction

Groundwater is any water found beneath the earth surface, including underground streams and water that fills the tiny spaces between soil and rock grains. Hydrologically, groundwater originates as infiltration from precipitation, rainfall, stream flows, lakes and reservoirs. The water seeps horizontally and vertically downwards into the soil through porous strata by gravity, until it reaches an impervious stratum, upon which it collects, forming groundwater [1]. During dry periods, it can also sustain the flow of surface water and even where the latter is readily available. Although groundwater is less contaminated than surface waters, pollution of this major water supply has become an increasing concern in recent decades due to contamination by various toxic substances [2].

The quality of any groundwater actually depends upon the types of materials on the seepage routes, the dissolved salts and the general human activities and the disposal systems. The flow path controls the movement of contaminants originating at the surface, and where the water table is shallow and the soil is porous, dissolved gases, nitrates, sulphates, metals, soluble organic compounds and dissolved salts may be introduced into the water system [3, 4]. Under a given hydraulic gradient, the more permeable the earth materials, the more will be the velocity of contaminants flow along the flow path. The presence of these contaminants in a groundwater above the World Health Organisation (WHO) standard can cause different kinds of ailments in humans that consume it, while higher concentrations are undesirable for industrial uses [5, 6].

Numerous intricate processes control the distribution of trace elements in groundwater, which typically has a large range of chemical composition [7]. The trace element composition of groundwater depends not only on natural factors such as the lithology of the aquifer, the quality of recharge waters and the types of interaction between water and aquifer, but also on human activities, which can alter these groundwater systems, either by polluting them or by changing the hydrological cycle [8, 9]. Sophisticated data analysis techniques are required to effectively interpret trace element data in groundwater. The univariate statistical analysis has been generally used to treat trace element data in groundwater. The simplicity of the univariate

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statistical analysis is obvious and likewise the fallacy of reductionism could be apparent. In order to avoid this problem in our study, multivariate method of cluster analysis (CA) is used to explain the multiple correlations amongst a large number of variables in terms of a small number of underlying factors without losing much information [10, 11]. The intention underlying the use of multivariate analysis is to achieve great efficiency of data compression from the original data, and to gain some information useful in the interpretation of the environmental geochemical origin. This multivariate treatment of environmental data is widely successfully used to interpret relationships among variables so that the environmental system could be better managed [12, 13].

The goals of the present study were to (1) access the pollution index by estimating the variations in physicochemical parameters in the groundwater samples; (2) investigate the statistical distribution and correlation of measured variables in the groundwater; (3) employ the multivariate statistical methods for the apportionment and identifications of pollution sources in groundwater. It is anticipated that the present study would help to identify and rectify the groundwater pollution problem in the metropolitan areas of Lahore and to motivate further explorative studies to this effect.

Results and Discussion

Statistical Distribution

The statistical distribution of the physicochemical parameters and selected metals are shown in Tables-1 and 2, respectively, followed by the comparison of the measured variables with international and national standards in Table-3. The correlation findings are displayed in Table-4, while Figs. 1 and 2 revealed the quartile distribution of the selected metals and dendrogram of the cluster analysis, in that order. The mean values of the physicochemical parameters in the groundwater samples along with other statistical parameter are shown in Table-1, which indicate the prevailing quality status of the groundwater system within the study area, and thus represent a baseline data with which future environmental performance could be measured. The pH values ranged between 7.50 and 8.20 with a mean value of 7.91. The water samples exhibited pH values within the World Health

Table-1: Statistical distribution of the physicochemical parameters in the groundwater (n=48).

	Min	Max	Mean	Median	SE	Skewness
pH	7.50	8.20	7.91	8.00	0.06	-0.44
Alkalinity (m.mol/L)	2.80	8.20	4.70	4.35	0.36	0.91
EC (μS/cm)	329	1090	642	604	56.1	0.62
TDS (mg/L)	198	762	442	417	40.6	0.53
Hardness (mg/L)	100	300	166	150	16.1	0.80
HCO_3^- (mg/L)	140	410	235	218	18.1	0.91
NO_3^- (mg/L)	0.70	2.00	1.18	1.10	0.11	0.73
Cl^- (mg/L)	9.00	90.0	24.4	15.0	5.34	2.35
F^- (mg/L)	0.18	0.33	0.22	0.20	0.01	1.77
SO_4^{2-} (mg/L)	17.0	104	53.7	47.5	6.69	0.51
PO_4^{3-} (mg/L)	0.05	0.13	0.10	0.09	0.01	-0.34
Turbidity (NTU)	0.46	3.95	1.38	0.96	0.23	1.60

Table-2: Statistical distribution of the selected metals in the groundwater (n=48).

	Min	Max	Mean	Median	SE	Skewness
Na (mg/L)	12	152	83.3	85	9.88	-0.3
K (mg/L)	1.3	5.7	3.35	2.85	0.37	0.33
Ca (mg/L)	14	72	31.5	30	3.89	1.15
Mg (mg/L)	11	34	20.9	18	1.99	0.55
Fe (mg/L)	0.01	2.32	0.77	0.69	0.19	0.63
Pb (μg/L)	0.26	7.1	2.22	1.82	0.47	1.28
As (μg/L)	24.6	71.6	36	32.8	2.82	2.29

Table-3: Comparison of average levels of physicochemical parameters and selected metals with national and international standards.

	Mean	WHO Guidelines	USEPA Standards	National Standards
pH	7.91	6.5-8.5	6.5-8.5	6.5-8.5
Alkalinity (m.mol/L)	4.70	--	--	--
EC (μS/cm)	642	--	--	--
TDS (mg/L)	442	1000	500	1000
Hardness (mg/L)	166	500	--	--
HCO_3^- (mg/L)	235	--	--	--
NO_3^- (mg/L)	1.18	10	10	50
Cl^- (mg/L)	24.4	250	250	--
F^- (mg/L)	0.22	1.5	4.0	1.5-4.0
SO_4^{2-} (mg/L)	53.7	250	250	--
PO_4^{3-} (mg/L)	0.10	--	--	--
Turbidity (NTU)	1.38	<5 NTU	<5 NTU	<10 NTU
Na (mg/L)	83.3	200	--	--
K (mg/L)	3.35	12	--	--
Ca (mg/L)	31.5	75	--	--
Mg (mg/L)	20.9	150	--	--
Fe (mg/L)	0.77	0.30	0.30	--
Pb (μg/L)	2.22	10	15	10-50
As (μg/L)	36	10	10	10-50
Reference	Present study	[5]	[14]	[15]

Organization (WHO) guidelines [5] and United States Environmental Protection Agency (USEPA) standards [14] as well as national standards for drinking water [15]. Low pH enhances the solubility of substances in water, some of which are toxic to human. Average values of electrical conductivity (EC) and alkalinity were 642 μS/cm and 4.70 m.mol/L, with the corresponding ranges of 329 to 1090 μS/cm and 2.80 to 8.20 m.mol/L, in that order.

Table-4: Correlation coefficient* matrix of physicochemical parameters and selected metals in the groundwater (n=48).

	pH	Alkalinity	EC	TDS	Iardness	ICO_3^-	NO_3^-	Cl^-	F^-	SO_4^{2-}	PO_4^{3-}	urbidity	Na	K	Ca	Mg	Fe	Pb
Alkalinity	-0.08																	
EC	-0.07	0.89																
TDS	-0.07	0.89	0.99															
Hardness	-0.15	0.48	0.72	0.71														
HCO_3^-	-0.08	0.99	0.89	0.89	0.48													
NO_3^-	-0.42	0.11	0.10	0.12	0.01	0.11												
Cl^-	-0.14	0.24	0.61	0.61	0.78	0.24	-0.22											
F^-	-0.18	-0.03	0.13	0.14	0.43	-0.03	0.24	0.38										
SO_4^{2-}	-0.03	0.73	0.92	0.92	0.75	0.73	0.11	0.73	0.30									
PO_4^{3-}	0.20	0.44	0.38	0.39	-0.01	0.44	0.09	0.03	0.23	0.46								
Turbidity	-0.24	0.32	0.42	0.41	0.46	0.32	0.15	0.35	0.47	0.46	0.03							
Na	0.05	0.86	0.83	0.84	0.23	0.86	0.11	0.23	-0.15	0.68	0.55	0.17						
K	-0.32	0.77	0.80	0.79	0.79	0.77	0.19	0.42	0.28	0.68	0.07	0.61	0.47					
Ca	-0.18	0.24	0.53	0.52	0.92	0.24	-0.13	0.83	0.33	0.61	-0.16	0.29	0.01	0.60				
Mg	-0.09	0.66	0.80	0.79	0.89	0.66	0.14	0.58	0.47	0.76	0.18	0.59	0.44	0.84	0.63			
Fe	-0.15	0.28	0.19	0.18	0.08	0.28	0.57	-0.29	-0.15	0.17	0.18	0.11	0.18	0.25	-0.09	0.23		
Pb	0.26	0.07	-0.07	-0.07	-0.36	0.07	-0.31	-0.30	-0.53	-0.23	0.14	-0.16	0.24	-0.20	-0.43	-0.18	-0.15	
As	-0.12	-0.26	-0.27	-0.26	0.06	-0.26	-0.05	0.00	0.07	-0.22	-0.51	-0.28	-0.45	0.01	0.26	-0.19	-0.39	-0.41

*bold values are significant at $p < 0.001$

Total dissolved solids (TDS) ranged between 198-762 mg/L with mean and median values of 442 and 417 mg/L, respectively. Generally, TDS values in the groundwater remained within WHO guidelines and national standards; only few samples exceeded the USEPA standards. Total hardness, which is mostly due to the presence of dissolved calcium and magnesium salts ranged between 100-300 mg/L, having values within the WHO permissible limit. None of the samples recorded values that fall within less than 50 mg/L soft water classification [16].

The bicarbonate (HCO3-) levels spread from 140 to 410 mg/L, with almost similar mean and median levels and symmetrical distribution. The concentration of nitrate (NO_3^-) was between 0.70-2.00 mg/L with a mean value of 1.18 mg/L. Lower nitrate levels compared to the WHO and USEPA limit of 10.0 mg/L were measured in all samples, thus the waters are considered safe for drinking with respect to nitrate. In groundwater, nitrates are contributed by leaching from septic tanks, sewage, fertilizer runoff and natural erosion. Low chloride (Cl^-) level of 9.00 to 90.0 mg/L compared to the WHO and USEPA limit of 250 mg/L was recorded for all the samples. Significant difference between mean and median levels (24.4 mg/L vs. 15.0 mg/L) as well as higher standard error (SE) and skewness values of chloride revealed its random distribution in the water samples. The fluoride (F^-) contents of the groundwater ranged from 0.18 to 0.33 mg/L, manifesting average concentration of 0.22 mg/L, which are within the national and international standards. Major sources of fluoride in groundwater included water additives, erosion of natural deposits, discharge from fertilizer and aluminium factories [14]. Average concentration of sulphate (SO_4^{2-}) was measured at 53.7 mg/L, ranging from 17.0–104 mg/L and was lower than the USEPA and WHO permissible limit of 250 mg/L in drinking water. Phosphate (PO_4^{3-}) concentration ranged between 0.05-0.13 mg/L. Although no available limit is set for phosphate, very high concentration in water could stimulate algae growth [7]. Physical examination of the data showed the values of turbidity ranging between 0.46-3.95 units, with mean and median values of 1.38 and 0.96 units, respectively.

The mean concentrations and other statistical distribution parameters of selected metals estimated in the groundwater samples are shown in Table-2. The concentrations of Na, K, Ca, Mg and Fe ranged between 12.0-152 mg/L, 1.30-5.70 mg/L, 14.0-72.0 mg/L, 11.0-34.0 mg/L and 0.01-2.32 mg/L, respectively. Lead (Pb) and arsenic (As) showed concentration ranges correspondingly in the order of 0.26-7.10 µg/L and 24.6-71.6 µg/L. On the average basis, trace metals revealed following decreasing order; Na > Ca > Mg > K > Fe > As > Pb, with the corresponding levels of 83.3 mg/L, 31.5 mg/L, 20.9 mg/L, 3.35 mg/L, 0.77 mg/L, 36.0 µg/L and 7.1 µg/L, respectively. In most of the cases, mean and median levels closely match with each other, thus reflecting relatively Gaussian distribution pattern. However, moderately higher values of SE and skewness evidenced somewhat unsystematic distribution in the metal concentrations in groundwater system. The concentrations of Na, K, Ca, Mg and Pb are within the WHO guideline values; however, As and Fe contents in the groundwater are

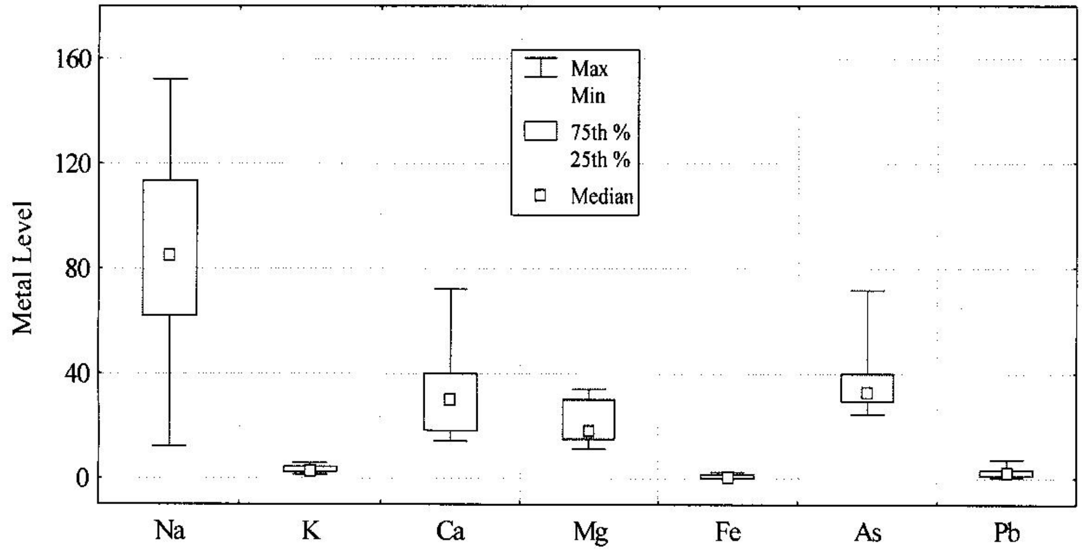

Fig. 1: Box-Whisker plot showing the quartile distribution of selected metals in the groundwater.

significantly higher than WHO and USEPA limits. The occurrence of some of the elevated metal levels in the samples reflected that their presence in the groundwater system is influenced by the soil or rock's mineralogy, as well as external environmental conditions. Water during its movement and storage in the earth acquires increased amounts of dissolved constituents including trace metals. Very high concentrations of these metals in drinking water are undesirable. Records of proven health effects ranging from gastrointestinal, respiratory and neurological disorders, decreased fertility, spontaneous abortion, low birth weight, cancer to instant death in some cases depending on the level of toxicity of the metals have been reported [6-18].

These observations are of concern as arsenic concentration in groundwater is prone to sharp fluctuation depending upon geochemical conditions. In groundwater, arsenic is reported to be contributed by runoff from glass and electronics production wastes, petroleum refining, wood preservatives, animal feed additives, herbicides, and erosion of natural deposits [14]. This analysis clearly reveals that presently groundwater is alarmingly contaminated with arsenic and its considerable disparity between mean and median levels, high standard error and large skewness indicated that the distribution is widely off normal. This was also manifested in the Box and Whisker (BW) plot where median and lower quartile almost fell on each other (Fig. 1). Positive skewness is also indicative of the asymmetric nature of the arsenic distribution in the groundwater. Elevated concentration of arsenic may cause skin damage or problems with circulatory systems, and may have increased cancer risk [14]. As shown in Fig. 1, almost symmetrical distribution for Na is evident from quartile division. However, K, Fe and Pb exhibited very narrow distribution while Ca and Mg showed relatively lopsided distribution in the present study.

Correlation Study

The close inspection of correlation matrix was useful because it can point out associations between variables that can show the overall coherence of the data set and indicate the participation of the individual chemical parameters in several influence factors, a fact which commonly occurred in hydrochemistry [8]. The findings of the correlation study are shown in Table-4 as correlation coefficient matrix, where only those r-values higher than 0.50 were considered significant. Among the physicochemical parameters, alkalinity, electrical conductivity, TDS, bicarbonate and sulphate are closely associated as manifested by very strong correlation coefficient values. These parameters are also strongly correlated with Na, K and Mg in the groundwater. As shown by the correlation relationships, bicarbonates and sulphates are the predominant contributor to the alkalinity of the

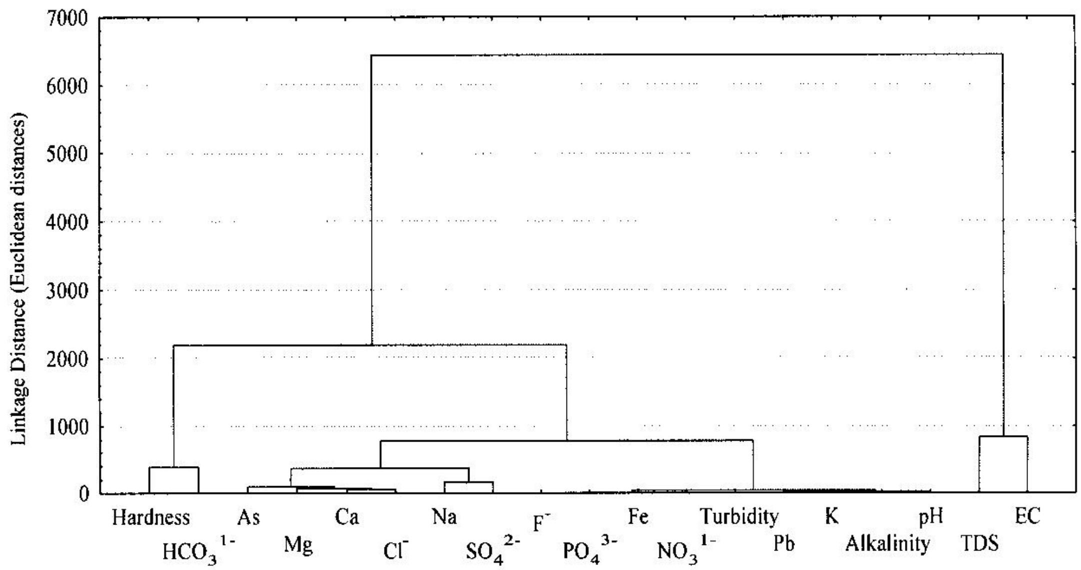

Fig. 2: Dendrogram (cluster analysis) of physicochemical parameters and selected metals in the groundwater.

groundwater in the present study. Electrical conductivity and TDS are mostly associated with the soluble salts of Na, K, Ca and Mg as manifested by the strong correlations among these variables. Relatively higher contents of the Fe in the present study are linked with the nitrates which exhibited significantly positive correlation with it. Likewise, chlorides are positively correlated with Ca and Mg thus reflecting a common origin. Inspection of Table-4 also showed that the trace elements, K, Ca and Mg are closely correlated. One interpretation of these observations was that these trace elements in groundwater had similar hydrochemical characteristics in the study area. The redox sensitive element, As, is very weakly correlated with other variables and no significant relationship with any other metal was observed. Generally, As is relatively more soluble in oxidized groundwater; however, in reducing waters, it is easily incorporated in insoluble minerals [19, 20]. Pb also revealed an independent variation pattern in the correlation study. Among other variables, pH, fluoride and phosphate also exhibited non-significant correlations with parameters.

Multivariate Cluster Analysis

Cluster analysis comprises a series of multivariate methods which are used to find true groups of data. In clustering, the variables are grouped such that similar variables fall into the same class [21]. Hierarchical cluster analysis is the most widely applied techniques in the earth sciences and is used in this study. Hierarchical clustering joins the most similar observations, and then successively the next most similar observations. The levels of similarity at which observations are merged are used to construct a dendrogram, as shown in Fig. 2. Some measure of similarity must be computed between every pair of variables. In this study, a standardized Euclidian distance is used: A low distance shows the two variables are similar or 'close together', whereas a large distance indicates dissimilarity. The physicochemical parameters and selected metals measured during the present study constitute four main groups as shown in the form of dendrogram in Fig. 2. The major group identified by cluster analysis is composed of fluoride, phosphate, Fe, Pb, K, nitrate, alkalinity, pH and turbidity and this group is believed to originate from the surface contaminants carried into the groundwater by slow seepage processes and mostly anthropogenic in origin. The second important cluster comprises Ca, Mg, As, chloride, Na, and sulphate which are mostly contributed by the geological processes and hence natural in origin. Another cluster is composed of bicarbonate and hardness and the two variables are directly associated with each other in hydrogeochemictry. Likewise, electrical conductivity and TDS constitute another cluster which is almost independent of other variables because it collectively represents the input of all cations and anions in the groundwater. The present study thus revealed the contribution of both natural and anthropogenic sources in the groundwater pollution.

Experimental

Sampling and Samples Preservation

Following a reconnaissance survey, and based on the available geophysical information forty-eight groundwater samples were collected from the tube-wells installed in the urban areas of the city. Sampling and sample preservation were done according to prescribed standard procedures [22, 23]. Samples for physicochemical parameters were put into 2 L pre-cleaned polythene kegs, while, samples for the trace metal analysis were collected into a 100 mL polyethylene narrow-mouth bottle with screw cap. Special care was taken to avoid contamination during sample collection, processing and transportation. Before sample collection, the bottle was rinsed at least three times with groundwater filtered through 0.45 mm mixed cellulose ester membrane. Samples were kept in an ice chest prior to the transportation to the laboratory where they were further preserved at approximately $4^{\circ}C$ before analysis.

Analysis of Samples

The physicochemical parameters of the groundwater samples were determined by the prescribed standard methods [22, 23]. pH, conductivity and total dissolved solids were measured at sampling points using portable Hannah meters. In the laboratory, the water turbidity was determined with a turbidimeter. Alkalinity, hardness, chloride and bicarbonate were determined titrimetrically, while phosphate, nitrate and sulphate were analyzed by UV-Visible spectrophotometer. Fluoride were estimated by ion-selective electrode, whereas, samples for selected metals were analyzed using an atomic absorption spectrophotometer [22, 23].

In the quality assurance program, both the international standard reference material (SRM 96) and the synthetic solutions were used for each batch of 10-sample analysis in order to verify the accuracy in the analytical procedures applied. Three replications of each analysis were performed and the mean values were used for calculations. The recovery of the standard reference material (SRM 96) was greater than 95%. The methods employed for the determination of the other species, not certified in the reference materials, were instead checked by preparing synthetic aqueous solutions. Inter-laboratory comparison of the data was also exercised at an independent laboratory and normally, a maximum of ± 5 % deviation was observed in the results of the two laboratories.

Conclusions

This study has presented the current quality characteristics of the groundwater within city, and serves as baseline data with which an impact of future development in the area could be monitored. Meanwhile, the present status of some of the waters does not meet the international quality standards with respect to some constituents, a condition that is likely to worsen in coming times. The mutual variations in measured variables are shown by the correlation statistics. The study also showed that the analysis of physicochemical data using the multivariate cluster analysis can give some information not available at first glance. Both natural and anthropogenic sources are significantly contributing to the groundwater pollution index as manifested by the cluster analysis.

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