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Statistics and Geo statistics in the Study of Heavy Metals Contamination in Groundwater of Shazand, Arak, Iran

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Abstract
Groundwater contamination is one of the most important environmental problems around the world. Among different contaminators affecting water resources, heavy metals are the main concern due to their strong toxicity even in low concentrations. Being aware of the vulnerability of groundwater to the contaminations is necessary for urban planning and management. The present research aims to investigate the changes of water quality in Shazand, Arak using cluster analysis and metals diffraction by the help of GIS. 10 groundwater wells with drinking function were selected and tested for sampling. Then, concentration of the metal (Ni, Co, Zn, Cu, Pb, and Cd) was measured by Polarography system and the results were compared with standard values ordered in WHO and the standards of Iran (IRIS). Finally, similar concentration maps for given metals was drawn by GIS and clustering analysis also was used for grouping variables. These results indicate the issue that further researches are needed to determine the resource of distribution of heavy metals' concentration.
Keywords: Geographical Information System, Groundwater, Heavy Metals, Eenvironmental Contamination.

Introduction

Water is one of the most important parts of plant and animals life, derived from two natural main resources: surface water, such as freshwater lakes, rivers, streams and groundwater such as well *(Gleick P. H., 2000)*. Regarding to the polarity and hydrogen bonds, water has unique chemical properties and is able to dissolve, absorb, and adsorb many compounds *(Butt, M. S et al; 2005 and Saravanan. V., 2001).* Water consumption in Iran is 96 billion cubic meters that 51 billion are supplied from ground water .Ground water resources are among the most important resources of drinking water and agricultural water supply *(Sharma, C. 2005)*. Therefore, due to the importance of these resources both as agriculture resource and drinking resource, investigation of their quality seems necessary *(Garg, V and Kaushik, P., 2006)*. Several factors come together to destroy water resources and we can hope for the future of resources only under protective actions *(Bouwer H., 2000).*

Nowadays, industrial growth and development for the promotion of per capita national income and providing welfare for the people of the society is the wish of all developing countries including Iran *(Shivkumar, K and Biksham, G. 1995).*The industries which are created for providing welfare of the society are considered as one of the factors threatening human life because of inattention and lack of observance of environmental issues *(Thangarajan, M., 1999 and Gowd, S. S.; Kotaiah, B. 2000)*. Ground water contamination is one of the most important environmental problems; among wide range of water contaminators, heavy metals are the main concern due to their strong toxicity even in low concentrations *(Buechler, S. and Mekala, G. D. 2005)*. Different types of heavy metals used by human are preserved in ecosystem and some of them appeared as toxic effects on human life *(Singh, G and Bhati, M. 2005)*. WHO has estimated that one fourth of human diseases is related to being subjected to environmental contaminations for a long time. Heavy metals are the elements with atomic weight of 63.546 to 200.59, and specific atomic weight of 4; which is 5 times more than water *(Abdulraheem, M. Y., 1989)*. Heavy metals entered to the environment through different ways, which should be investigated by scientific and research methods. Cluster analysis is a statistical method that allows us to interpret the spatial relationships between objects or variables to detect groups. Among Geo statistical methods, GIS one of the best technologies simplifying the analysis and access to a wide variety of information. The use of GIS in water resources has been increasing in order to emphasize the importance of GIS in water resource management, related applications, and effective research and development in the future. The present study was designed to investigate the concentration of Heavy metals in groundwater (drinking) using statistical method through cluster analysis and Geo statistical methods.

Materials and methods

To do so, we first attempted to collect and study available scientific and applied references in this field. Sampling was conducted from 10 wells in the study area. For sampling, a Polyethylen which was already rinsed by concentrated nitric acid was used *(Bouwer, H.*

2000). In order to prevent from the precipitation of heavy metals, 1ml of concentrated nitric acid was added to 100ml of the sample *(Singh , G et al .; 2001 and Behera, B.and Reddy, V. R. 2002)*. Sampling method and maintaining the samples was performed according to the recommendations of Wastewater experiments standards book, 21st volume *(Chandra, R et al.; 2004)*. Preparation of each metal standards was conducted by diluting Tetrazole materials (Merck) with 1000 mg per liter of concentration *(Gupta, S. K.and Deshpande, R. D. 2004).* The measurement of heavy metals' concentration was conducted by Metrohm 797 Polarography system and using available methods in Metrohm application bulletin. Study area is Shazand in Arak province.

Description of the study area

Shazand County is one of the central counties. The center of the city, the town of Shazand is 33 kilometers southwest of Arak. This city, is abutting with Hamadan and Lorestan provinces which has mountainous climate.

Table 1. The position of sampling areas

Samples	Geographical Position		
Well 1	32° 13' 29" N	40° 98' 40" E	
Well 2	32° 14' 38" N	40° 98' 30" E	
Well 3	32° 14' 99" N	40° 97' 67" E	
Well 4	33° 43' 70" N	40° 97' 45" E	
Well 5	33° 42' 50" N	40° 97' 10" E	
Well 6	33° 05' 95" N	41° 19' 90" E	
Well 7	31° 85' 11" N	40° 96' 714" E	
Well 8	31° 50' 58" N	41° 11' 96" E	
Well 9	32° 91' 25" N	41° 48' 80" E	
Well 10	31° 77' 03" N	41° 30' 54" E	

Results and discussion

The occurrence of ground water contamination and the quality of ground water have become major issues since the discovery of numerous hazardous waste sites in the late seventies. An engineering hydrologist today must be able to address mechanisms of ground water flow, contaminant transport, biodegradation and sorption, pure phase impacts in source areas and plumes, and remediation schemes. Sources of ground water contamination are widespread and include thousands of accidental spills, landfills, surface waste ponds, underground storage tanks, pipelines, injection wells, land application of wastes and pesticides, septic tanks, radioactive waste disposal, salt water intrusion, and acid mine drainage.

Table2. The concentration of heavy metals in water samples (mg/L)

Sample	Zn	Cd	Pb	Cu	Ni	Co
Well 1	2/425	0/318	0/800	0/386	1/077	0/630
Well 2	3/532	0/261	0/813	1/641	3/912	0/675
Well 3	2/580	0/218	0/771	0/557	0/928	0/674
Well 4	2/642	0/147	0/812	1/574	1/650	0/640
Well 5	2/523	0/224	0/687	1/553	1/908	1/554
Well 6	2/212	0/180	0/752	1/030	4/959	0/554
Well 7	2/355	0/111	0/652	1/269	1/126	0/760
Well 8	2/520	0/055	0/362	1/998	1/036	0/719
Well 9	3/086	0/140	1/005	1/354	1/578	0/718
Well 10	2/314	0/102	0/457	2/288	1/270	0/718
Minimum value	2/212	0/055	0.362	0.386	0.928	0.070

The concentration of heavy metals in water samples were determined by using Polarography and is given in Table 1. The data Show that heavy metals are observed in all the samples but in all cases are less than the maximum allowable value of World and Iran standards and follows as below:

Zn> Ni> Cu> Co>Pb> Cd.

Cluster analysis also clearly shows the relationship between the amount of metals based on the similarity or dissimilarity to clustering method in separated groups. It can be concluded from this grouping that which are the metals with a common source. Zonation maps also show distribution pattern of these metals in regional level. According to the values obtained using GIS, the zoning map of heavy metals' concentration was provided.

Drawing Chernoff'sfaces for water samples allows us to determine some of clear differences between the samples in a glimpse. Figure 1 shows that water samples are very different in terms of heavy metal content. To determine the difference between effective factors, clustering analysis was used.

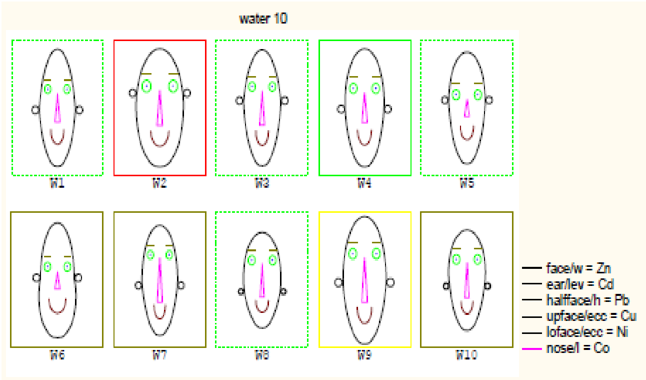

Figure1. Chernoff's drawings related to the concentration of 6 heavy metals in water samples

Figure 2 shows that metal ions of Cadmium, Nickel, Copper, Zinc, and Cobalt are in similar clusters and have common resource. It shows that the main difference between water samples are influenced by the 2 groups of variables. To estimate contamination level, Geostatistics method also was used.

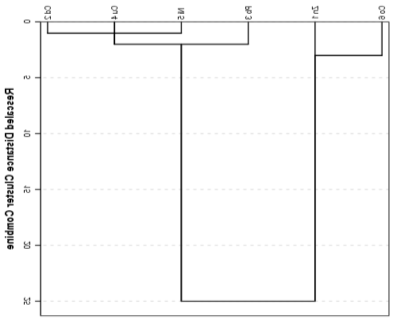

Figure 2. Heavy metals clustering in water samples

Assessment of groundwater pollution potential in a given drinking water catchment may be conducted under a wide variety of conditions and at varying spatial scales and levels of sophistication *(Foster, S.S.D and Hirata, R. 1988).*This broad variation means that assessments of pollution potential can require an equally broad range of sophistication, ranging from reconnaissance surveys of the major potential sources of groundwater pollution to detailed surveys of chemical or microbiological pollutant loads and even to simple modelling of, for example, the leaching potential of pesticides used in the catchment. This implies that experienced professionals from the hydrogeology and environmental engineering disciplines will normally be needed, both to help decide on the level of sophistication required, and to undertake the assessment itself. For some diffuse sources of pollution, semi-quantitative estimates of the likely concentrations of persistent pollutants in local recharge may be possible, given many simplifying assumptions *(Foster, S.S.D and Hirata, R. 1988)*. Approaches to doing this have been developed for chloride and nitrate from unsewered sanitation and for nitrate and pesticides from cultivated land *(Foster, S.S.D et al., 2002)* and are illustrated in the case studies at the end of the chapter.

A method that has been successfully applied is to use the distinctive isotopic signatures of nitrogen from animal and human excreta and from inorganic fertilizers to characterize the nitrate observed in the groundwater *(Heaton, T. H. E.1986; Aravena, R et al., 1993; Exner M. E and Spalding, R. F 1994; Rivers C. N et al., 1996)* and hence its origin. The distinctions are not, however, always unambiguous as denitrification can also modify the isotopic signature of the nitrate in groundwater. Alternatively, trace elements associated with high groundwater nitrate concentrations, such as zinc and boron, or pharmaceuticals, may be indicative of a sewage rather than an agricultural source *(Lerner D. N and Barrett, M. H. 1996).* Where an observed or anticipated pollutant may have originated from numerous small sources as, for example, in a large industrialised city, especially one with a long and complex industrial history, then it is likely to be technically difficult and unrealistically expensive to determine the precise origins, locations and characteristics of pollution sources *(Rivett, M. O et al., 1990; Ford, M and Tellam, J. H 1994)* In such circumstances efforts are better directed at protection and control of all potentially hazardous sources rather than trying to prove the precise origins of the pollution.Groundwater nitrate concentrations of 4-8 mg NO3-N/l were observed everywhere in the rural areas of both catchments, indicating universal but modest impact from agriculture, but there was no evidence of an overall increasing trend during the five years of the study or indeed when the results of the continuing groundwater quality monitoring programme were reviewed later by Chilton et al. (1998).Water quality surveys have detected a wide range of contaminants in shallow private boreholes near many of these sites, commonly at levels that exceed national drinking water criteria. Although this groundwater is generally not used for drinking, other routes of exposure, such as droplet inhalation or eating irrigated produce have not been thoroughly assessed. Groundwater contamination in at least one private borehole was sufficiently severe to be toxic on prolonged skin contact and to kill plants irrigated with the water *(Appleyard, S.J.1995).*There is also widespread leaching of nitrate from fertiliser use on gardens, and of nitrate, ammonia, and bacteria from septic tanks. Estimates of pollutant loading suggest that about 1600 tonnes of nitrogen and 480 tonnes of phosphorus is applied annually to lawn areas in Perth *(Pionke, H.B et al., 1990).*The results indicate that the disposal of industrial effluents on land, which has limited capacity to assimilate the pollution load, has led to groundwater pollution. However, this is a preliminary study and further detailed and comprehensive studies are required. The continuous application of polluted groundwater for irrigation has resulted in the increased salt content of soils. In some locations drinking water wells (deep bore wells) also have a high concentration of salts.The study shows that the environmental impacts of industrial effluent irrigation is different for different sites, which is mainly due to the fact that different industries have different pollution potential; and different locations have different assimilative capacities to absorb the pollutants. However, the degree of severity of the pollution is also a crucial factor which determines the feasibility to adopt averting behavior. This study shows that adoption of precautionary measures (averting behaviour) could mitigate the environmental problems related to pollution. The less stringent effluent discharge standards for land application may have motivated the industries to buy land and use effluents for irrigation. This is a direct threat to the soil quality. It is not only water use that must be placed under control. Land use also has implications for water and environmental quality. The close linkages between land and water in the basin means that a degradation in one of them will also infringe on the other with potential repercussions on human health, yields, product quality, aquatic ecosystems and, generally, socioeconomic opportunities and sustainability. Sustainable access to safe drinking water is one of the main targets of the United Nations Millennium Development Goals, and indiscriminate disposal of industrial effluents on land and surface water bodies make water resources unsuitable for drinking. Unlike developed countries, developing countries like India should follow the precautionary approach to protect the drinking water sources from point and non-point sources of pollution, as it cannot afford (financially and technically) to go for curative measures. Safe disposal of industrial effluents can support the achievement of this target. Water is a scarce resource. Thus, any reuse of water is desirable, as long as the costs (both direct and indirect) associated with the reuse is less than the benefits of using it. Detailed cost–benefit studies (both environmental and human health hazards) are essential before going in for industrial effluent irrigation.

Conclusion

Optimal management of water resources and also maintain and improve their quality requires available data on the location, amount and distribution of water chemical agents in a specific geographic region. According to the results of Heavy metals measurements, it can be said that lead, zinc,nickel, cadmium, cobalt and copper are present in 100% of the samples. Yet, their amount is not higher than the standard value in none of the samples. Therefore, the wells in this area of Arak Province are not contaminated by heavy metals. Zoning maps show that cobalt, nickel and lead are more in the Northeast, and copper ion in the Northwest; and zinc ions has a constant trend in the study area. Statistical analysis revealed relationship and correlation of the metals in studied samples.

These results indicate the issue that further researches are needed to determine the resource of distribution of heavy metals' concentration.

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