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Concentration of heavy metals in groundwater and heavy metal pollution index in Punjab

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Abstract
Groundwater samples (263 number) were collected from the Punjab state during August, September, and October, 2019 and were analyzed for heavy metals arsenic (As), aluminium (Al), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), and lead (Pb). It has been found that majority of the samples have concentrations within the acceptable limits as prescribed by Indian drinking water standards. The analysed data was used for calculating heavy metal pollution index (HPI) for groundwater and mean HPI was 4.9 which are well below the critical index limit of 100. On the basis of values of HPI, all samples were classified under 3 categories as low, medium and high for corresponding HPI values of <15, 15-30 and > 30, respectively. It was found that 2 samples have values > 30, 4 samples have HPI values in the range of 15-30 and all other samples have values < 15. The study based on HPI values demonstrated that heavy metal concentrations evidently indicates the groundwater of Punjab in majority of the area monitored, to be free from heavy metal pollution and can be used for human consumption. Groundwater in the areas where HPI index is > 15 may be avoided for drinking purposes and continuous monitoring is essential to check the heavy metal pollution.

Keywords: Heavy metals, Heavy metal pollution index, groundwater, Punjab

Introduction

Groundwater is the largest freshwater renewable resource used for drinking, irrigation and in industrial sector. Increasing demands of the freshwater exerting stress on this resource and is resulting in depletion of water levels and deterioration of water quality (MacDonald et al. 2016; Krishan et al., 2020, 2021a). Water quality is degraded due to addition of pollutants like microbes, salts (Krishan, 2019) other chemical (Krishan et al., 2021b) and trace metals (Krishan et al., 2021c). Presence of trace metals in groundwater not only affects water quality but also poses a serious threat to human health and socio-economic development (Milovanovic 2007). These heavy metals may dissolve in groundwater from (i) weathering of minerals (Karbassi et al. 2007); (ii) disposal of effluents containing toxic metals from different industries and (iii) usage of heavy metal rich fertilizer and pesticides in agricultural fields (Ammann et al. 2002; Nouri et al. 2008). These trace metals are required in optimum doses but it become fatal once it exceeds the critical level. Therefore, its monitoring is significant in the context of human health.

A single pollution parameter measurement gives an idea about the pollution due to the specific parameters but for understanding of overall pollution of a particular system, quality indices are quite useful (Mohan et al., 1996). Water quality indices have been used by many researchers for assessing water quality (Giri and Singh, 2014; Krishan et al., 2016; Singh et al., 2015, 2017, 2019; Yadav et al., 2015). Heavy metal pollution index (HPI) is a useful tool for assessing the heavy metal contaminations, where it rates the individual contaminant in a cumulative manner and provides overall quality with respect to heavy metals (Giri and Singh, 2014).

Punjab is an agrarian state with intensive cultivation where feritilizers and pesticides are used indiscriminately to get higher yields (Lapworth et al., 2017). There is high possibility of mixing of the contaminants from fertilizers and pesticides in groundwater. Therefore, present study was carried out to assess groundwater quality by computing HPI by measuring concentrations of trace metals viz. Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb in groundwater and compare the observed concentrations of metals with the drinking water quality guidelines/standards and identify the vulnerable areas with high concentrations of heavy metals.

Study Area

The present study was carried out in the Punjab State of India (Fig. 1). It is located between the geographical co-ordinates of Northern latitudes 29° 32' and 32° 28' and Eastern longitudes 73° 50' and 77° 00'. The Punjab state is bordered by Pakistan in the west, Haryana and Rajasthan in the south, and Himachal Pradesh in the North-east. Punjab constitutes 50, 362 sq. km of area. There are three perennial rivers namely Satluj, Beas and Ravi and one seasonal river, Ghaggar and the surface water potential of Punjab is 17.93 BCM, which is not sufficient to meet the requirements and hence looking towards utilization of groundwater resources. The total groundwater draft of Punjab is 35.78 BCM, against the availability of 21.58 BCM leading to over-exploitation of this resource.

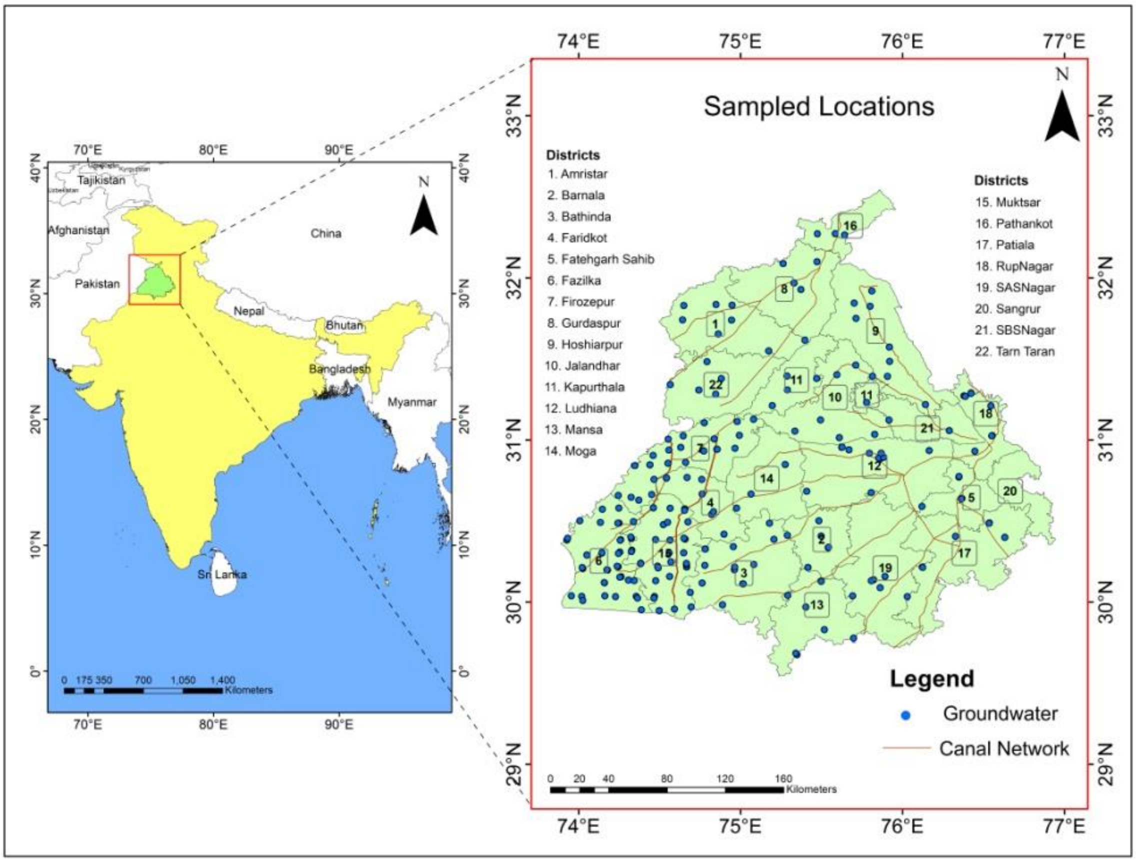

Fig. 1 Study area map showing sampling locations.

Rainfall

Rainfall is one of the main contributors to groundwater sources. The land with the steeper slope has less possibility for rainwater to infiltrate whereas the land surface with gentle or no slope has greater possibility of infiltration. The mean rainfall data have been analysed from the year 2000 to 2019 (Fig 2). It was observed that 79% of rainfall occurs during June to September months.

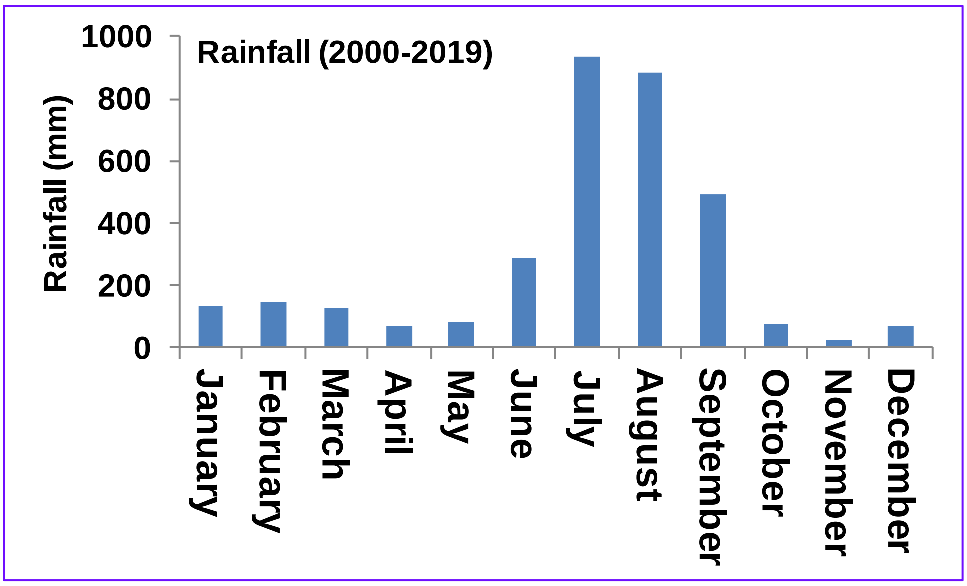

Fig. 2 Average monthly rainfall during 2000-2019 in Punjab.

Landuse/Landcover

The quality and the quantity of groundwater depend mainly on the type of the land. The SENTINEL-2 MSI satellite data of kharif season, 2019 was used for the classification. The supervised classification has been done by ERDAS Imagine software, by training the algorithm with sample datasets. The whole state was classified into five landuse/landcover classes such as Surface water (1%), Agricultural land (73%), Fallow land (7%), Settlements (16%), Hilly area/forest (3%) (Fig. 3a).

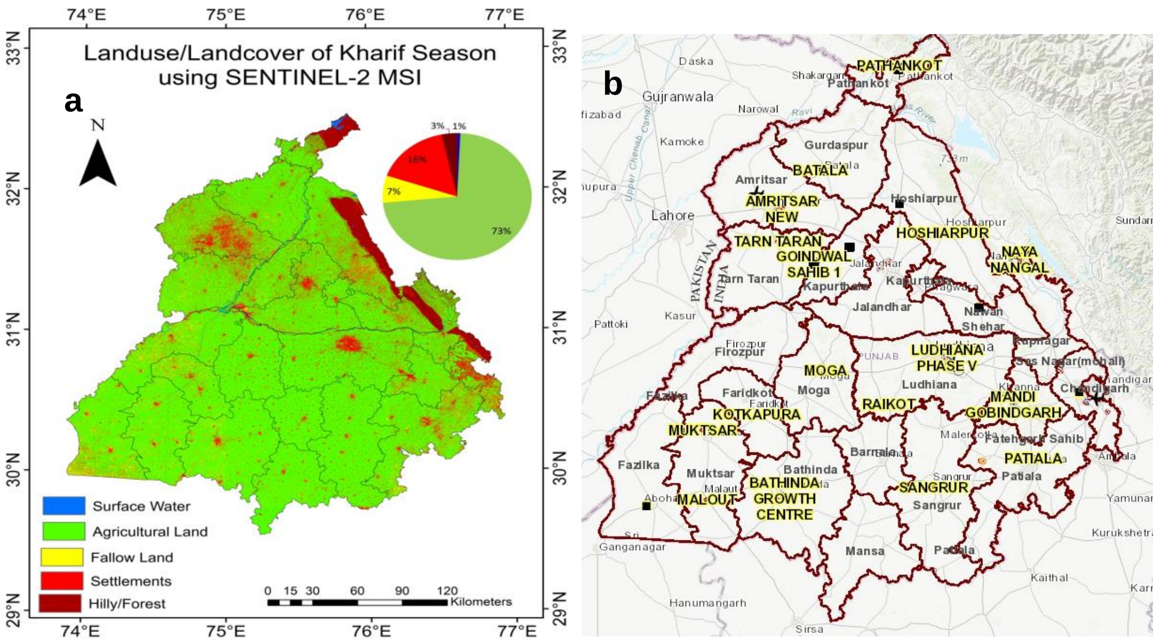

Fig. 3 (a) Landuse/land cover map and (b) locations of industries in Punjab.

Punjab being an agrarian state, consumption of the fertilizers is about 180 kg/hectare which is considered very high, about 10 times of the national average. Fertilizers used in Punjab largely pertain to nitrogen, phosphorus, potassium, calcium, magnesium, sulfur and micronutrients categories. In addition to the agricultural discharges, Industrial effluent discharge is also one of the main reasons for heavy metal concentration in groundwater. The locations of the main industrial areas in Punjab have been shown in the figure 3b. There are about 1.9 lakh small industries and more than 500 large and medium units operating in Punjab state. In Punjab, major industries are: (i) agriculture sector - food processing, tractors and auto components, agro-based parts; (ii) others- textiles, bicycle and bicycle parts, sports goods, light engineering goods, metal and alloys, other chemical products. District Ludhiana leads the industrial output in Punjab.

Hydrogeology

The surface elevation map has been prepared from the SRTM-DEM satellite data (Fig 4a). From the elevation data it is clear that the higher elevation was found in the North-eastern region of Punjab (Siwalik range) which continues to decrease in south west direction. The lithology data have been obtained from the Geological survey of India (Fig 4c). The most prevailing litholog type in Punjab state was found to be Oxidised silt-clay with kankar and micaceous sand, the surroundings of the river were dominated by Grey micaceous sand, silt and clay.

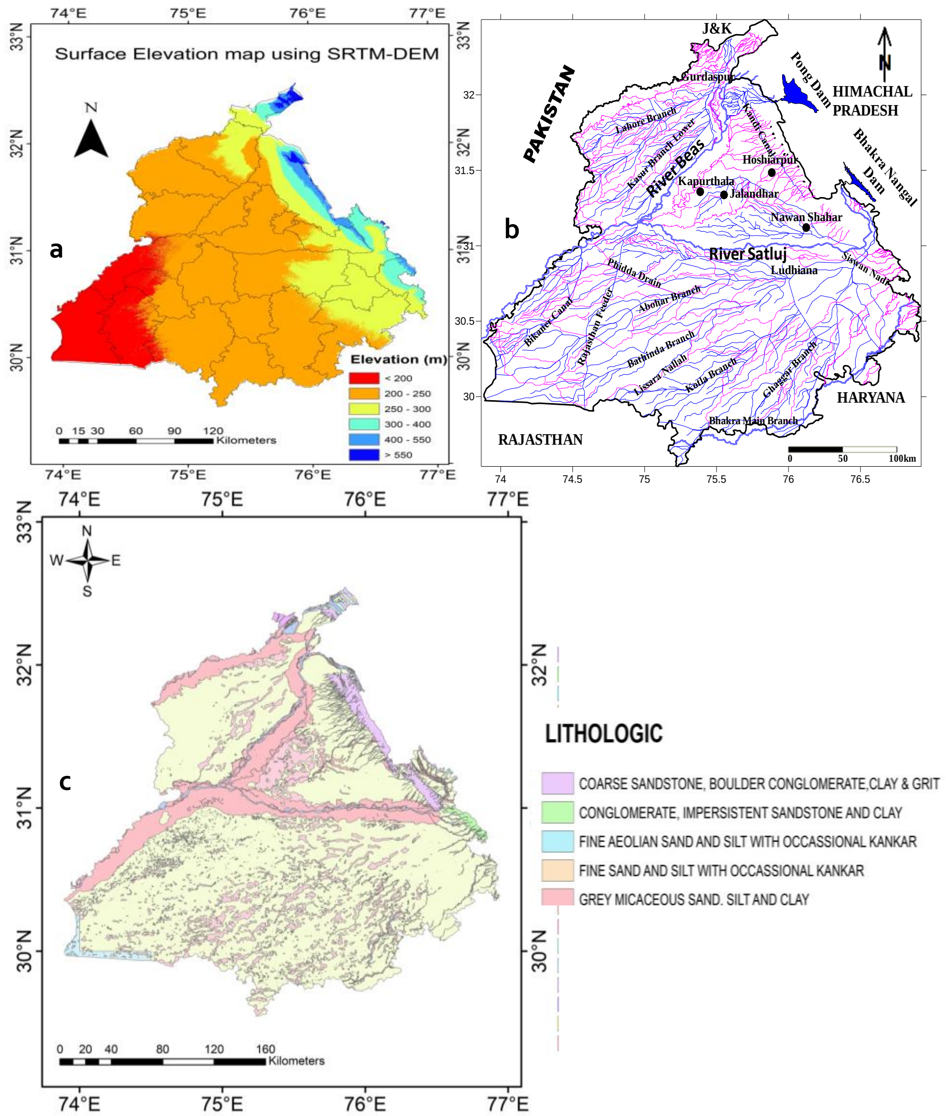

Fig. 4, a, b, c, DEM, drainage map and lithology of the Punjab.

The Punjab state is mainly underlain by Quaternary alluvium of considerable thickness which is capable of sustaining heavy duty tube wells (CGWB, 2017). Laterally and vertically extensive thick fresh water regional aquifers are found in the entire state. In some parts there are localized and discontinuous aquifers (CGWB, 2017). The block-wise groundwater data has been collected from Central Groundwater Board (CGWB, 2017) and district wise statistics have been computed (Fig. 5). The overall stage of groundwater development is very high bout 166% which implies that the annual ground water consumption is more than annual groundwater recharge. The highest percentage of stage of groundwater development of 260% was found in Sangrur district, whereas the lowest percentage of 74% was found in Muktsar district.

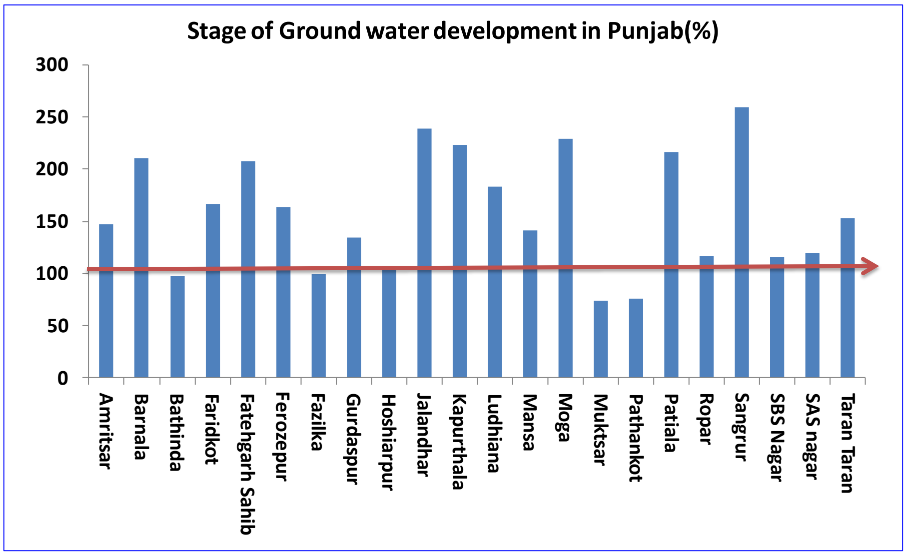

Fig. 5 Stage of groundwater development in Punjab.

Materials and Methods

Sample collection

The sample collection for heavy metal analysis has been carried out in all districts of Punjab. Fazilka, Muktsar and Firozepur districts have been sampled intensively and in other parts of Punjab coarse sampling has been carried out. All of the groundwater samples were taken with hand pumps and tube wells, which are widely used. Depth of these groundwater structures ranged from 5m to > 350 m. A portable global positioning system was used to establish the location of each sampling site. The sampling sites were selected so as to ensure that all drinking water wells having potable water are covered. In the study area, groundwater is typically consumed without treatment.

To get the proper sample, pumping was done for 10-15 minutes before sampling. During the sampling period, the weather was reasonably consistent. On-the-spot measurements were taken, including the position, source, and depth of the hand-pumps. The water samples were filtered to extract suspended matter/sediments using 0.45 µm millipore nitrocellulose filters (disposable, not reusable), acidified to pH 2 (0.2 percent v/v) using supra pure nitric acid (HNO_3) for preservation, and then preserved in pre-cleaned acid-washed high density polyethylene (HDPE) containers before study.

Sample Analysis

The samples were analysed as per Standard Methods for the Examination of Water and Wastewater (APHA, 2012; Jain and Bhatia, 1988). All measurements were made with an Agilent 5100 SVDV ICP-OES with Dichroic Spectral Combiner (DSC) technology, which analyses vertically oriented plasma in both axial and radial views at the same time. A seaspray nebulizer, single-pass glass cyclonic spray chamber, white pump tubing, and a regular 1.8 mm injector torch made up the sample introduction scheme. The instrument uses a solid state RF (SSRF) system operating at 27 MHz to deliver robust plasma capable of excellent long term analytical stability. This is a high speed (1MHz) CCD detector that enables fast warmup, high throughput, high sensitivity, has a large dynamic range of up to 8 orders of magnitude and provides full wavelength coverage from 167–785 nm from a single entrance slit. The wavelengths of the respective elements along with their minimum detectable limit have been tabulated below (Table 1).

Table 1 Trace metal detection wavelength and Minimum Detectable Limit (MDL) of the instrument

Element	Wavelength (nm)	MDL (µg/L)
Arsenic	188.980	0.5
Cadmium	228.802	0.4
Chromium	267.716	0.7
Copper	327.395	0.4
Iron	238.204	0.4
Lead	220.353	3.0
Manganese	257.610	0.1
Nickel	231.604	3.1
Zinc	213.857	1.1

Single element standards were diluted with 1 percent HNO_3 to make the standards. The following trace metals in drinking water (TMDW) Certified Reference Materials (CRM) were analysed to validate the method: TMDW-A and TMDW-B. (High Purity Standards, Charleston, South Carolina, USA).

Table 2 Acceptable and Permissible limit as per BIS, 2012 drinking water standards

Trace Metals	BIS 10500:2012 Acceptable Limit	BIS 10500:2012 Permissible Limit
Aluminium (ppm)	0.03	0.2
Arsenic (ppm)	0.01	0.05
Cadmium (ppm)	0.003	-
Chromium (ppm)	0.05	-
Copper (ppm)	0.05	1.5
Iron (ppm)	0.3	-
Manganese (ppm)	0.1	0.3
Nickel (ppm)	0.02	-
Lead (ppm)	0.01	-
Zinc (ppm)	5	15

Heavy Metal Pollution Index (HPI)

The heavy metal pollution index (HPI) is a ranking system and a useful tool for determining the quality of water in terms of heavy metals (Hafez and Zakhem, 2015; Sheykhi and Moore, 2012). This was used to represent the combined influence of metals on the overall quality of water (Reza and Singh 2010; Reza et al. 2011). Many researchers have used HPI index for the surface water analysis. The study of HPI in groundwater was presented by the Yankey et al. (2013) and Kumar et al. (2012).

$$HPI = \frac{\sum_{i=1}^{n} W_i * Q_i}{\sum_{i=1}^{n} W_i} \text{ - - - - eq} \qquad (1)$$

Where,

Q_i = Sub index of the i^{th} parameter

W_i = The unit weight of the i^{th} parameter and n is the number of parameters considered.

The sub index (Q_i) of the parameter is calculated by

$$Q_i = \sum_{i=1}^{n} \frac{(M_i - I_i)}{(S_i - I_i)} \, x \, 100 \text{ - - - - eq} \qquad (2)$$

Where,

M_i = Monitored value of heavy metal of the i^{th} parameter
I_i = Ideal value of the i^{th} parameter
S_i = Standard value of i^{th} parameter

HPI values demonstrated heavy metal concentrations free from heavy metal pollution and can be used for human consumption. Groundwater in the areas where HPI index is >15 may be avoided for drinking purposes and continuous monitoring is essential to check the heavy metal pollution.

Result and Discussion

Heavy metal concentrations

The samples were tested for the Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni) and Zinc (Zn). The statistical parameters including the minimum value, maximum value, average and the standard deviation were tabulated for respective Heavy metals (Table 3).

Table 3 Statistical parameters of Heavy metal in analysed groundwater samples

Statistical parameters (ppb)	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Min	0.35	0.01	0.03	0.02	10.00	0.22	0.01	0.02	24.22
Max	68.61	1.36	85.19	47.35	6830.0	1026.48	9.04	37.72	4789.41
Ave.	6.70	0.13	1.48	1.83	251.66	38.43	1.23	0.93	260.14
S.D.	10.99	0.18	6.05	5.40	691.68	105.12	1.38	3.02	396.32

The concentration of arsenic in groundwater ranges between 0.35 and 68 ppb. High arsenic is found in Majha region (Krishan et al., 2021c). The highest concentration was found in Gatti village, Ferozepur district. The maximum concentration of chromium is upto 85.19 ppb with an average of about 1.47 ppb. The iron in the samples was measured upto 6830 ppb with an average of 251 ppb. The manganese measured from 0.22 to 1026 ppb with an average of about 38.4 ppb. Excess iron and manganese concentrations are due to their presence in earth's crust (Kumar et al. 2010; Senapaty and Behera 2012).

Heavy metal pollution index (HPI)

The combined effect of agricultural pesticides and Industrial pollutants increased the heavy metal pollution in the Groundwater. Even though each and every single parameter of the heavy metals have been analysed and mapped separately, the study of combined effect for heavy metals is very much essential.

The HPI values have been calculated for each and every sampling site by substituting the analysis results in the above mentioned equation (2) to calculate Q_i which have been substituted in the equation (1) to calculate Heavy metal Pollution Index (HPI). The results along with the geographic co-ordinates have been interpolated using ArcGIS to obtain the spatial distribution across the districts of Punjab. The HPI value in the study area ranges from 0.07 to 37.23 with an average of about 4.87.

The HPI values mapped was grouped into five classes from low (< 5) to high (> 30) (Kumar et al. 2012). The HPI values above 15 have been considered as threat for the groundwater. From the HPI spatial distribution map, it is clear the main hazardous zones have been found in the Firozepur and Ludhiana districts. In Firozepur, it is found in the Harike (Junction of Sutlej and Beas river) and Acche wala village. High aluminium, iron and manganese contribute to the high HPI values in Firozepur district while higher iron, manganese and chromium contents contribute to higher HPI values in Ludhiana districts. The less hazardous threat zones (HPI from 10 to 15) have been found in the parts of Gurdaspur, Ludhiana, Fazilka, Muksar, Mansa and Rupnagar districts. Heavy metal contamination has been found to be within limits in the remaining areas of Punjab.

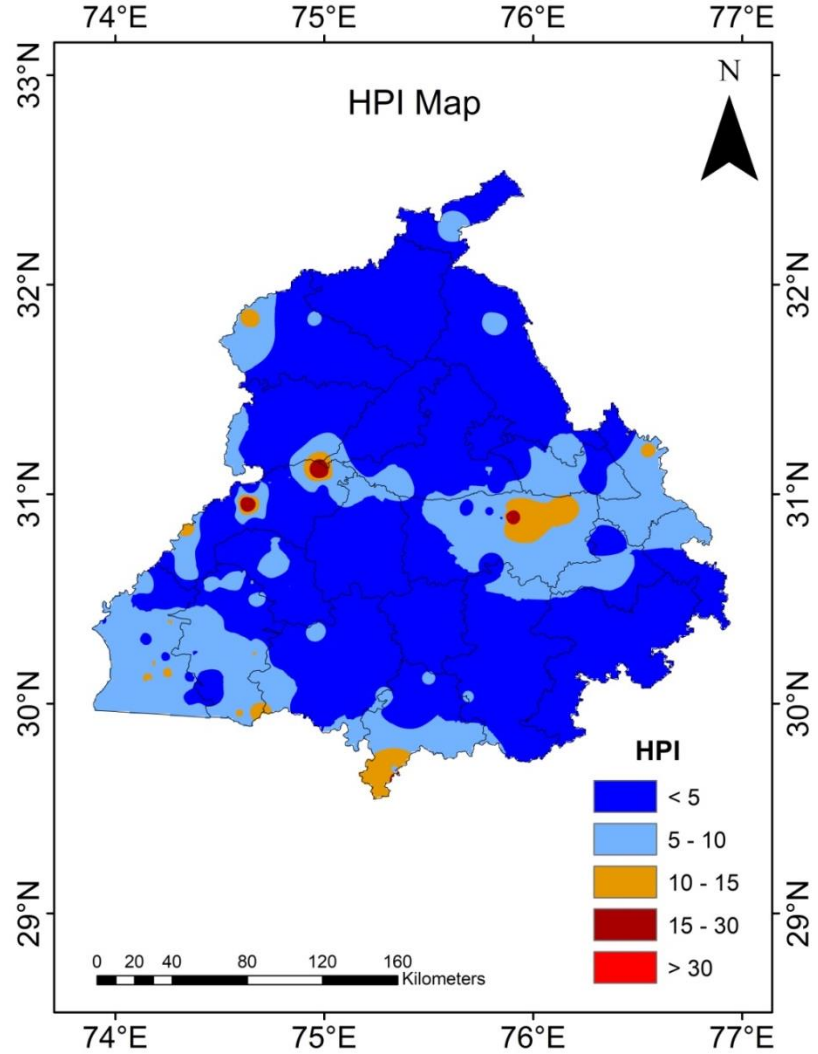

Fig 6 Heavy metal pollution index of groundwater in Punjab.

Conclusions

HPI values have demonstrated that the groundwater of Punjab is free from heavy metal pollution and can be used for human consumption. Higher HPI values are due to elevated concentrations of iron, manganese are found in the industrial areas of Firozepur and Ludhiana districts. However, groundwater in the areas where HPI index is > 15 may be avoided for drinking purposes and continuous monitoring is essential to check the heavy metal pollution.

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References

Ammann AA, Michalke B, Schramel P (2002) Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. Analytical and Bioanalytical Chemistry 372(3):448–452

Bureau of Indian Standards (BIS). Drinking water-specifications, 2nd revision of IS 10500; BIS: New Delhi, India, 2012.

Giri S, Singh AK (2014) Assessment of surface water quality using heavy metal pollution index in Subarnarekha River, India. Water Quality Exposure and Health (London) 5(4):173–182

Karbassi AR, Nouri J, Ayaz GO (2007) Flocculation of trace metals during mixing of Talar river water with Caspian Seawater. International Journal of Environment Research 1(1):66–73

Krishan, G. (2019). Groundwater Salinity. Current World Environ 14(2):186-188

Krishan, G, Kumar, C.P, Purandara, B.K., Singh, Surjeet, Ghosh, N.C., Gurjar, Suman and Chachadi, A.G. 2016. Assessment of variation in water quality index (WQI) in north Goa, India. Current World Environment. 11(1): 39-46.

Krishan, G, Prasad, Gokul, Anajli, Kumar, C.P., Patidar, Nitesh, Yadav, Brijesh, Kansal, M.L., Singh, Surjeet, Sharma Mohan, Lalit, Bardley, Allen, Verma, S.K. 2020. Identifying the seasonal variability in source of groundwater salinization using deuterium excess- a case study from Mewat, Haryana, India. Journal of Hydrology- Regional Studies, 31: 100724 https://doi.org/10.1016/j.ejrh.2020.100724

Krishan, G, Vashisth, Rajesh, Sudersan, N, Rao, M.S. (2021a). Groundwater salinity and isotope characterization: a case study from south-west Punjab, India. Environmental Earth Science, 80, 169. https://doi.org/10.1007/s12665-021-09419-7

Krishan, G, Sejwal, P, Bhagwat, A, Prasad, G, Yadav, B.K, Kumar, C.P., Kansal, M.L., Singh, S,, Sudarsan, N, Bradley, A, Sharma, L.M, Muste, M. (2021b). Role of Ion Chemistry and Hydro-Geochemical Processes in Aquifer Salinization—A Case Study from a Semi-Arid Region of Haryana, India. Water. 13(5):617. https://doi.org/10.3390/w13050617

Krishan, G, Rao, M.S., Ghosh, N.C., Kumar, B, Kumar, C.P., Sharma, A, Singh, S, Kumar, S, (2021c). Expansion of salinization in aquifers of Punjab. Report submitted to Punjab State Farmers and Farm Workers Commission, Punjab. 155pp

Kumar S, Bharti VK, Singh KB, Singh TN (2010) Quality assessment of potable water in the town of Kolasib, Mizoram (India). Environmental Earth Science 61(1):115–121

Kumar PJS, Delson PD, Babu PT (2012) Appraisal of heavy metals in groundwater in Chennai city using a HPI model. Bulletin of Environment Contaminationa and Toxicology 89:793–798. doi:10.1007/s00128-012-0794-5

Lapworth, DJ, Krishan, G, MacDonald, AM, Rao, MS. (2017). Groundwater quality in the alluvial aquifer system of northwest India: new evidence of the extent of anthropogenic and geogenic contamination. Science of the Total Environment. 599–600 (2017) 1433–1444

MacDonald, A, Bonsor, H , Ahmed, K, Burgess, W, Basharat, M, Calow, R, Dixit, A, Foster, S, Krishan, G, Lapworth, D , Lark, M, Moench, M, Mukherjee, A, Rao, M.S., Shamsudduha, M, Smith, L, Taylor, R, Tucker, J, Steenbergen F , Yadav, S, (2016). Groundwater depletion and quality in the Indo-Gangetic Basin mapped from in situ observations. Nature Geosciences. 9:762-766.

Mohan SV, Nithila P, Reddy SJ (1996) Estimation of heavy metal in drinking water and development of heavy metal pollution index. Journal of Environmental Science and Health 31(2):283–289

Nouri J, Mahvi AH, Jahed GR, Babaei AA (2008) Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environmental Geology 55(6):1337–1343

Reza R, Singh G (2010) Assessment of heavy metal contamination and its indexing approach for river water. International Journal of Environmental Science and Technology 7(4):785–792

Reza R, Singh G, Jain, M K (2011) Application of heavy metal pollution index for ground water quality assessment in Angul district of Orissa, India. International Journal of Research in Chemistry and Environment 1(2):118–122

Senapaty A, Behera P (2012) Concentration and distribution of trace elements in different coal seams of the Talcher Coalfield, Odisha. International Journal of Earth Science and Engineering 5(01):80–87

Sheykhi V, Moore F (2012) Geochemical characterization of Kor River water quality, Fars Province, Southwest Iran. Water Quality Exposure and Health 4:25–38

Singh S, Ghosh, N.C., Krishan G, Galkate R, Thomas T. and Jaiswal R.K. (2015). Development of an Overall Water Quality Index (OWQI) for Surface Water in Indian Context. Current World Environment. 10(3): 813-822

Singh, S, Ghosh, N C, G, Suman, Krishan, G, Kumar, S, Barwal, P. (2017). Index-based assessment of suitability of water quality for irrigation purpose under Indian conditions, Environment Monitoring and Assessment. 190:29

Singh, S., Ghosh, N.C., Krishan, G., K Sumant, G, Suman, S, MK. (2019). Development of indices for surface and ground water quality assessment and characterization for Indian conditions Environment Monitoring and Assessment. 191: 182.https://doi.org/10.1007/s10661-019-7276-8

Yadav KK, Gupta N, Kumar V, Sharma S, Arya S (2015) Water quality assessment of Pahuj River using water quality index at Unnao Balaji, MP, India. The International Journal of Sciences: Basic and Applied Research 19(1):241–250

Yankey RK, Fiank JR, Osae S, Ahialey EK, Duncan AE, Essuman DK, Bentum JK (2013) Evaluation of heavy metal pollution index of groundwater in the Tarkwa mining area, Ghana. Elixir Pollution 54:2663–12667

Zakhem BA and Hafez R (2014) Heavy metal pollution index for groundwater quality assessment in Damascus Oasis, Syria. Environmental Earth Science 73:6591-6600.