Socioeconomic and recharge effect on spatial changes in the groundwater chemistry of Punjab, Pakistan: a multivariate statistical approach

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Abstract

This study presents deterioration in groundwater quality of highly populated region of Punjab Province, Pakistan, by linking chemical data with rain, river recharge, and socioeconomic factors. Various chemical parameters like total dissolved solid (TDS), arsenic (As), fluoride (F^-), Iron (Fe), nitrate (NO_3^-), nitrite (NO_2^-), and pH were determined for 46,457 samples collected from 205,344 km² area of the Punjab. The samples were collected, stored, and analyzed as per the Environment Protection Agency (EPA) methods at laboratory. Commercial kits were used for analysis of Fe, As, NO_2^- , NO_3^- and F^- , while TDS and pH were measured by respective meters. Chemical parameters were correlated with human and animal population, fertilizers consumption, tube wells, industrial density, rain occurrence, and river recharge rate. Data were analyzed using XLSTAT, and GIS 10.3 was used to draw the maps. Spatial classification of the districts was performed by principal component analysis and hierarchical cluster analysis. TDS, As, F^- , Fe, NO_3^- , NO_2^- , and pH were found to be 50–52,360 mg/L, 0–735 µg/L, 0–121 mg/L, 0–37.2 mg/L, 0–2215 mg/L, 0–3033 mg/L, and 0.09–10.9, respectively. The study revealed that 66.26% of the samples were fit for drinking purpose, while 33.74% were unfit. Further, it was found that 27% of the samples were non-saline, 26% were saline, and 47% were slightly saline based on the World Health Organization drinking water quality criteria. A nonlinear model was developed which explains 57% of variance in groundwater quality. Based on groundwater quality, the whole province was divided into three main regions: northwestern districts, central districts and southeastern districts. Central Punjab was highly polluted, followed by southeast region, while northwest Punjab has better quality water due to more rains and Indus River. Current study provides a model to predict future water quality of the region and suggests that new water canals in southeast Punjab can improve water quality. Moreover, it is recommended that agriculture and industrial effluents should be controlled to improve water quality, new smart cities should be built along Indus River, and population should be controlled in southeast and central Punjab.

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Graphical abstract

Keywords Punjab · Groundwater · Arsenic · Nitrate · Nitrite · Fluoride

1 Introduction

Punjab is a part of upper Indus basin, and during the past two decades, its groundwater chemistry has been changed significantly [1–3]. Shallow ground water in Punjab is 20–200 feet below the ground surface and is used for drinking, agriculture, industrial activities, and farming. Current challenges of the Punjab groundwater are: depletion [4, 5], salinization [6], mobilization of arsenic (As), fluoride (F^-) [7], uranium (U) [8], and nitrate (NO_3^-) [9]. Substantial number of samples were found in the eastern Punjab region having traces of toxic pollutants (Pb, Cr, Ni, Cd, Cu, As, Fe, F^- , and Mn) with higher concentration than the WHO limits [2, 10, 11]. Lahore and Kasur groundwater is severely contaminated with F^- and As, and 20–70% of the samples from Lahore have higher F^- level than 1.5 mg/L [12]. Another study showed 19% samples from Punjab have higher NO_3^- than WHO level of 10 mg/L [11]. A survey of 383 villages of Punjab showed 23% samples have As greater than 10 $\mu\text{g/L}$, while 11% exceed 50 $\mu\text{g/L}$. Most of these villages lie across River Ravi which has been dried up after promulgation of Indus water treaty [13]. Maximum value of As and F^- in east and south Punjab districts was 906–1000 $\mu\text{g/L}$ and 2.8–8.6 mg/L, respectively [14, 15]. Drinking of polluted groundwater has resulted in dental, skeletal fluorosis, hyperthyroidism (goiter), methemoglobinemia, gastric cancer, goiter, birth malformations, and hypertension in the region [16–19].

Geological studies revealed anthropogenic sources are polluting groundwater, as shallow aquifer has high As [20] and F^- than deep aquifer [21]. Therefore, it is expected that socioeconomic sources are playing more significant role in controlling groundwater quality than geochemical factors [21–24]. Fertilizer consumption has been increased manifold in the last three decades. Such excessive use of fertilizers in various agricultural areas of Punjab played a vital role in groundwater pollution. Two to three decades ago, F^- in groundwater was related to arid conditions or natural rocks weathering, as fluor spar, cryolite, fluorapatite, and hydroxyapatite were found in local rocks [17–19, 25–27]. Later studies changed the narrative of sources, as sulfate (SO_4^{2-}), As, and F^- were detected in rain [28]. Industrial waste, household water, and coal burning are source of As and F^- as maximum values of 2400 $\mu\text{g/L}$ and 22.8 mg/L have been reported near an industrial zone in Lahore which decreases away from zone [21, 22]. Local diammonium phosphate (DAP) and coal contain F^- 25–255 mg/L [28] and 5–20 mg/L, respectively, while same DAP contains As 5–10 mg/Kg [22, 23]. Nitrogen (NO_3^- vs. N) data also show that animal waste has contributed to nitrate

pollution. These anthropogenic sources contributed significantly to the rising level of phosphate (PO_4^{3-}), SO_4^{2-} , NO_3^- , As, F^- , Fe , NO_2^- and carbonate (CO_3^{2-}) in groundwater [17, 22, 24].

Rawalpindi, Kasur, and Bahawalpur groundwater contains Ca^{2+} – HCO_3^- , Na^+/K^+ – HCO_3^-/Cl^- and Na^+/K^+ – HCO_3^-/SO_4^{2-} as dominating ions, respectively [15]. $Na^+Cl^-/Na^+HCO_3^-$ type groundwater [15] with higher F^- , As, and NO_3^- as common contaminants is reported in many eastern and south Punjab [29]. High $Na^+HCO_3^-$ water is formed by silicate and carbonate weathering and evapotranspiration at high pH in addition to anthropogenic factors (agriculture return, domestic sewage, and fertilizer) [18, 28] and promotes F^- and As dissolution [22] with low Ca^{2+} and Mg^{2+} [29], low NO_3^- , high Fe and SO_4^{2-} [29]. Higher As and F^- in shallow groundwater than in deep groundwater are found in south Punjab [29] which is different from east Punjab, Lahore [28]. Release of As in east Punjab may be due to reductive dissolution of $FeO(OH)$ with dissolved organic matter (natural or anthropogenic from animal or agriculture) [20], while south Punjab As release can be due to oxidative/evaporative mechanism, in addition to phosphate interaction at high pH [29]. Saline intrusion is also result of water tube well extraction [28, 30]. Rock–water interaction is accelerated with aquifer overexploitation which might have enriched F^- and As in the deep groundwater [15] as observed in some wells in south Punjab [31].

Currently, Ravi and Sutlej have less than 2 MAF average water flow near Balloki and Sulemanki barrages, while it was 10–12 MAF in 1980. Indus, Jehlam, and Chenab have average annual flow of 62, 23, and 25 MAF with seasonal variation, and decreasing volume trend is observed till present; as a result, water deficit is reported in 25 main canals [32]. Canal irrigation system raised water table during British era [33, 34], while current agriculture practices has lowered the water table due to water abstraction at rate of 2.1 $\text{km}^3 \text{yr}^{-1}$ [35]. Local recharge is also reduced due to construction of cemented water channels to provide water to tail end farmers. Groundwater quality is generally fresh along the rivers except in Bari Doab (Ravi and Sutlej Rivers in Bari Doab are dried and carry sewage water) and deteriorates as it moves away from the rivers toward the central parts of the Doabs [2, 36, 37].

After Indus water treaty, river hydrology and recharge patterns have been changed and rate of socioeconomic development varies in different districts [35, 39–41]; therefore, comparative impact of these changes on groundwater quality should be determined at macroscopic level rather than site-specific studies. There are 36 districts in

Punjab while past studies are mostly focused on specific sites in few districts, especially Bari Doab or central Punjab, while less data are available of western districts [37, 38]. Current study is conducted to determine groundwater trace pollutants: As, F^- , Fe, NO_3^- , NO_2^- , pH, and TDS (salinity) of all village/towns of 36 districts and compare with socioeconomic factors like tube wells, population, animal population, fertilizer consumption, industries per square kilometer of respective region. The comparison will reveal relative pollution in these districts and their relation with the anthropogenic sources. This study aims to determine spatial variation of groundwater quality based on recharge from various sources and provides a model to predict changes in groundwater salinity in the future. Current research enhances understanding that change in river hydrology due to India–Pakistan water treaty has influenced groundwater pollution significantly in addition to anthropogenic sources of pollution.

2 Materials and methods

2.1 Study area

Punjab has population of 110,012,442, and it borders with Sindh toward south, Khyber Pakhtunkhwa toward the west, Baluchistan toward southwest; Islamabad, Azad Jammu and Kashmir toward north. It borders with Indian state of Punjab and Rajasthan toward east (Fig. 1a). It is located between latitude 27.42° – 34.02° north and longitude 69.18° – 75.23° east. Total land area is 205,344 km² which contributes 25.8% of the total land of Pakistan. It stretches 1078 km north to south and 616 km from east to west [39].

2.2 Hydrogeology

Punjab is covered by 200 m alluvium originated from Himalaya underlain by Precambrian basement rock [28]. Unconfined aquifer of Punjab has alluvial plain comprising more than 350 m thick Holocene and Pleistocene sediments transported by Indus and tributaries [40, 41] directly overlain by the metamorphic, sedimentary, and igneous rocks of Precambrian age [2, 6]. These sediments consist of fine to very fine sand and low organic matter [42]. Area between Sutlej and Ravi is called Bari Doab, between Ravi and Chenab rivers, Rechna Doab; Chenab and Jehlam Rivers, Jech Doab; Jehlam and Indus Rivers, Sind Sagar Doab [42].

2.2.1 Eastern rivers

There were five rivers flowing through Punjab before 1960, and one river flows along border districts (Indus River). River Jehlam joins Chenab at Trimmu near Jhang. Both join Ravi at Sidhnai near Ahmedpur Sial. Beas River joins Sutlej at Kapurthala and Sutlej–Beas joins Jehlam–Chenab–Ravi at Uch near Bahawalpur to form Panjnad. Punjab has semi-arid and subtropical continental climate with sultry summers and cold winters [28].

2.2.2 Western rivers

Gilgit River joins Indus near Juglot, and Kunar and Swat join Kabul River near Jalalabad. Combined stream of Kabul joins Indus near Attock. Kurram River (320 km) joins Indus near Isa Khel. Gomai joins Zhob near Khajuri Kach, and combined stream of Zhob stretches 161 km and joins Indus near Dera Ismail Khan [43, 44]. Combined stream of Sutlej–Beas–Ravi–Chenab–Jehlam stretches 45 km south-west and joins Gilgit–Kabul–Kurram–Zhob–Indus stream at Mithankot to form mighty Indus River. Mighty Indus passes through Rajanpur and Rahim Yar Khan (R-Y-Khan) before entering Sindh Province.

2.2.3 Surface water budget

Mangla (near Jehlam) and Chasma (near Mianwali) lakes are located inside Punjab. Chenab and Jehlam have 48.68 million acre feet (MAF) of total flow; Indus at Kalabagh (near Mianwali) has 89.71 MAF during summer; Ravi and Sutlej at Balloki & Sulemanki have 4.23 and 2.59 MAF of maximum flow during summer. Total escape to sea is 39–50 MAF [43]. There are 23 major canals stretches over 34,500 km having capacity of 65 billion cubic meter surface water. Punjab has 13 barrages, 2 siphons, and 10 link canals (Rasul–Qadirabad, Qadirabad–Balloki, Balloki–Sulemanki, Trimmu–Sidhnai, Sidhnai–Mailsi, Mailsi–Bahawal, Chasma–Jehlam, Taunsa–Panjnad link-canals). There are 135 surface drainages including 670 drains, with total length of 6600 km which drain 5.79 million hectares. During 1999–2000, total irrigated area was 13.8 million hectares, out of which 11 million acres are in canal command [45, 46].

2.2.4 Aquifers

Pothwar plateau (Jehlam, Chakwal, Rawalpindi, and Attock) has separate confined groundwater aquifer [47, 48]. Baluchistan and southwest Punjab also separated through Sulaiman range [35]. Northwestern, western, and southeastern Punjab aquifer is not connected to outside; however toward north and northeastern side, aquifer is

Fig. 1 **a** Current study area of the Punjab, Pakistan, for groundwater quality. **b** Samples location and number of samples from various districts

extended and it forms unconfined aquifer [10]. Total recharge is 42.75 MAF, and it includes 9.90 MAF rainfall recharge, 21.70 MAF canal system, 7.08 MAF irrigation return, 3.50 MAF river recharge, and 0.57 MAF domestic and industrial return flow. Total tube well discharge is 31.50 MAF, domestic and industrial discharge is 2.50 MAF, and 8.75 MAF is losses. Total discharge is 42.75 MAF [49]. According to a recent estimate, total ground water abstraction is 50 MAF with 1 million tube wells [46].

2.3 Data acquisition and mapping

Punjab is administratively divided into districts, tehsils, and towns/villages. Samples were collected from front, center, and backside of each town/locality. Three samples were taken from each village and averaged for that locality. Total 46,457 samples were collected from whole Punjab Province during January 2014 to December 2016 (Fig. 1b). TDS and pH were measured with TDS and pH meters, made of Hanna Instruments model HI98192 and HI98190, respectively right after sampling. Other chemical moieties (As, F^- , Fe, NO_3^- , and NO_2^-) were analyzed in the laboratory [50, 51] with kits made of ChemMetrics. Rain data were collected from regional meteorological stations. Population, industries, livestock, fertilizers, and tube wells data were taken from statistical pocket book of the Punjab government [52] and converted to density data (per km^2) after dividing by the area of each district. Socioeconomic density and rain data were used to discuss groundwater quality pollution. All chemical, hydrological, and socioeconomic parameters have been mapped using GIS, version 10.3.

2.4 Data mining

Hierarchical cluster analysis (HCA) is an exploratory data mining technique that extracts and classifies data into various groups [53–56]. HCA was performed after z transformation by Ward's method with Euclidean distance as measure of similarity using XLSTAT [57–59]. Districts of the Punjab were classified into three groups by HCA and principal component analysis (PCA), [53, 57, 58] based on water quality parameters (TDS, As, Fe, F^- , NO_3^- , NO_2^- , and pH), socioeconomic parameters (human and animal population, fertilizers sale, tube wells, industrial density), and climate parameters (rain, river recharge) [60]. Guildford's rule of thumb was applied for interpreting correlation coefficients [60, 61].

2.5 Predictive modeling

Various socioeconomic factors affect groundwater quality; therefore, multiple nonlinear regression model was

selected [62–64] to predict influence of each factor on TDS in the future. A generalized nonlinear model was applied (Eq. 1) using 3 degree polynomial to predict overall water quality parameters (TDS) for given values of socioeconomic/climate parameter. Equation 1 [62, 63, 65] is valid unless seepage rate from the rivers and streams remains at current level.

$$Y = pr1 + pr2 \times X1 + pr3 \times X2 + pr4 \times X3 \dots \quad (1)$$

3 Results and discussion

Various elements' concentration was determined including As, F^- , Fe, NO_3^- , NO_2^- , and pH (Fig. 2). Most of the ions (F^- , Fe, NO_3^- , and NO_2^-) average values were high than WHO limits in certain districts (Tables 1, 2, and 3 in supporting information). Based on WHO drinking level criteria, 66.26% samples were fit, while 33.74% were unfit for drinking [66–70]. Close observation of spatial maps (Fig. 2) for all parameters (Fe, F^- , As, and TDS) show two main pattern of distributions, i.e., southeast side (along India border) has more deteriorated water than northwestern side (bordering Khyber Pakhtunkhwa (KPK), Gilgit-Baltistan (GB), and Azad Kashmir). Water quality is better in those districts where Indus, Jehlam, and Chenab Rivers are flowing. Previous studies have reported fresh water up to 50 km area around Indus and its tributaries [2, 10], while areas around Ravi and Sutlej Rivers have deteriorated groundwater quality.

3.1 Main contaminants

Mean, median, and mode values of As for Punjab were 12.83, 5.00, and 0.00 mg/L, respectively (Table 1) [28, 66]. Indus gigantic basin (IGB) has As < 10 $\mu g/L$ [2], and current studies found As 0–735 $\mu g/L$ in Punjab. A survey reported 3% of Punjab population is exposed to As > 50 $\mu g/L$ [66], while 20% population is exposed to As > 10 $\mu g/L$ [71, 72]. Shallow water study in 2001 revealed 9% samples contain As > 10 $\mu g/L$ [66], whereas 0.7% of samples contain > 50 $\mu g/L$ [28]. Samples (46,457 samples) analyzed in current study are more than in previous studies, and it was found that 2.53% samples have As > 50 $\mu g/L$, while 8.07% have As > 10 $\mu g/L$. Higher As is already reported in cities around rivers: Lahore [73], Kasur, Bahawalpur, Sahiwal, R-Y-Khan, Muzaffargarh [71], while current study (Fig. 2, Tables 1, 2, and 3 in supporting information) found mode of Lahore, Muzafar Garh, and Kasur was 50 $\mu g/L$, 50 $\mu g/L$, and 10 $\mu g/L$, respectively. Maximum value of As in Kasur and Muzafar Garh districts is 906–1000 $\mu g/L$ [14, 15].

Fig. 2 a–g Spatial distribution of (mean values) As ($\mu\text{g/L}$), F^- (mg/L), Fe (mg/L), NO_2^- (mg/L), NO_3^- (mg/L), pH, and TDS (mg/L) of Punjab, Pakistan

Arsenic in groundwater can be present due to both natural and anthropogenic factors. Arsenic may release from earth crust due to geological settling [10, 71], argillaceous and organic matter with fine-medium sands of Holocene alluvium [74–76]. Arsenic is desorbed from metal surface to the groundwater due to alkaline environment, as southeast have mostly alkaline groundwater [73]. Arsenic in shallow water is found to be higher than in groundwater because of anthropogenic sources like coal, diammonium phosphate [22] fertilizer, hydrofluorocarbon, and trifluoromethyl pesticide [22]. Detection of As in rain also verifies that commercial activities are releasing the metal [28]. Positive correlation coefficient (Table 2) was found between As versus industries (0.33), human population density (0.38), animal population density (0.31), and fertilizers (0.40); while negative correlation was found between As versus rain (-0.22). Current studies correlation data suggest that As is significantly contributed by commercial sources.

Mean, median, and mode of F^- of Punjab were 0.74, 0.52, and 0.00 mg/L , respectively (Table 1). Mean F^- was 1.51 and 5.51 mg/L in Khushab and Narowal, respectively (Table 1 in supporting information, Fig. 2b). In Punjab as a

whole, 10.63% samples were found to have $\text{F}^- > 1.5 \text{ mg/L}$ while 45.77% sample found to have $\text{F}^- > 0.5 \text{ mg/L}$. Maximum WHO limit is 1.5 mg/L [67], and it was alarming that significant percentage was higher than WHO limit [12]. Positive correlation was found between F^- versus rain (0.17), tube well density (0.39), and fertilizers (0.18) (Table 2). High values of F^- were found in southeast side (Fig. 2).

Mean, median, and mode of Fe of Punjab were 0.13, 0.04, and 0.00 mg/L respectively (Table 1). Samples having Fe $> 1 \text{ mg/L}$ were 0.42%, while samples having Fe $> 0.1 \text{ mg/L}$ were 15.27%. Punjab Fe range was 0–37.20 mg/L and positive correlation was found between Fe vs. animal density (0.16), and fertilizer sale (0.31). Highest average Fe was 1.02 mg/L in Sahiwal (WHO limit $\leq 1 \text{ mg/L}$), while Gujrat (0.61 mg/L), Rajanpur (0.34 mg/L), Chiniot (0.29 mg/L), Gujranwala & Nankana Sahib (0.28 mg/L each), Pakpattan (0.27 mg/L), Sialkot and Okara (0.24 mg/L each) also have higher values.

Mean, median, and mode of NO_3^- of Punjab were 9.93, 0.00, and 0.00 mg/L , respectively (Table 1). Samples have $\text{NO}_3^- > 50 \text{ mg/L}$ were 1.33%, while samples having $\text{NO}_3^- > 10 \text{ mg/L}$ were 10.48% as compared to previous

Fig. 2 (continued)

reports that showed 19% of samples exceed 10 mg/L. Current study sampling points are more than previous study (399) [11]; therefore, it is reliable. Many districts (47.2%) have mean NO₃⁻ greater than WHO limit (Table 1 in supporting information) [68]. Highest mean NO₃⁻ was 49.94 and 55.04 in Okara and Sialkot, respectively. Fresh water sources have less NO₃⁻; as central Himalaya, oceans, and rivers have 0.56 mg/L, 0.67 mg/L, and 1 mg/L [77]. Positive correlation coefficient of 0.24, 0.31, 0.36, 0.19, and 0.12 was found between NO₃⁻ versus rain, industries, tube wells, population density, and animal density, respectively. The highest sale of fertilizer was recorded in Okara in 2013–2014, and high NO₃⁻ in Okara can be due to high rate of application of agriculture fertilizer and Maize/corn cultivation. High-NO₃⁻ districts lie in southeast side than in northwest (Fig. 2e). Fertilizer consumption in southeast Punjab is higher than in northwest part. Boiler industry can contribute higher NO₃⁻ [78] due to higher population in southeast than in northwest. Concentration of nitrates can be high due to flood irrigation/rain seepage [79, 80] of fertilized land, animal waste, septic tanks and sewage dumps leaching [11].

Mean, median, and mode of NO₂⁻ of Punjab were 0.82, 0.00, and 0.00 mg/L, respectively (Table 1).

Samples having NO₂⁻ > 3 mg/L were 0.92%, while samples having NO₂⁻ > 1 mg/L were 3.82%. NO₂⁻ was found in 0–3033 mg/L range in the Punjab Province. District-wise mean NO₂⁻ was 53.16, 73.99, 4.20, 5.5, and 2.87 in Jehlam, MB-Din, Narowal, Pakpattan, and TT Singh, respectively. There are two distinct groups of district where NO₂⁻ was high, but these were not geographically connected and belong to different aquifers. As NO₂⁻ was positively correlated with rain (0.30) and tube well density (0.27), it is suspected that NO₂⁻ in Jehlam is due to water logging, while high NO₂⁻ in Pakpattan might be due to flood irrigation and agriculture practices.

Mean, median, and mode of pH of Punjab were 7.59, 7.50, and 7.40, respectively for 46,457 samples (Table 1). pH range was found in range of 0.09–10.90, while north-western side has less pH than southeastern side. Samples having pH > 7 were 81.84%, showing overall alkaline trend. Only 1.1% samples do not fall into WHO pH limit as 0.2% had pH > 9.2, while 0.90% had pH < 6.5. Previous studies suggested alkaline pH due to meteoric origin of the groundwater [73]. pH was negatively correlated with rain (−0.27) and tube wells (−0.37) similar to TDS. As southeast is more alkaline than northwest, it is suggested in addition

Fig. 2 (continued)

to natural factors, socioeconomic factors are also contributing to alkaline pH.

TDS comprises all dissolved inorganic ions (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) and dissolved organic matter [70, 81] and represents overall water quality. Food and agriculture organization (FAO) classifies water as non-saline when TDS is < 500 mg/L; slightly saline 500–1000 mg/L; saline 1000–2500 mg/L and highly saline when TDS is > 2500 mg/L [82]. WHO suggests < 600 mg/L is good quality, while it specifies 1000 mg/L as upper drinking limit [69, 83].

Mean, median, and mode of TDS of Punjab were 862.67 mg/L, 700 mg/L, and 560 mg/L (Table 1). Current study found samples having TDS > 1000 mg/L were 26%, while samples having TDS ~ 500–1000 mg/L were 47% and TDS < 500 mg/L samples were 27%. Punjab TDS range was found to be 50–52,360 mg/L. Southeast side has high values than northwest side (Fig. 2). Another study about IGB showed 23% samples have salinity > 1000 mg/L [2, 10]. Previous studies showed TDS of Lahore was 442–2573 mg/L and two-third samples in Lahore had higher TDS due to Na–Cl type water, while one-third is due to Na– HCO_3 [12]. Positive correlation coefficients were found between TDS

vs. industrial density (0.40), human population (0.19), animal population density (0.24), and fertilizer sale density (0.53), while negative correlation coefficient was found for rain (–0.28). Previous studies suggested meteoric origin of water is cause of higher TDS, in addition to socioeconomic factors found in the current study [73].

3.2 HCA

Hierarchical cluster analysis (HCA) has divided districts into three classes based on mean and median (Tables 3 and 4, Fig. 3). Districts around Indus River, especially Sind Sagar Doab, Pothwar and western side, were put into class 2 (non-saline), while districts between River Ravi and Sutlej (Bari Doab), Chenab and Ravi (lower Rechna) and lower Jech Doab (downward to Sargodha) were put into class 1 (slight saline). Okara and Faisalabad that are districts of worst quality water, were put into third class (saline).

This classification proved that water streams and rain are affecting overall groundwater chemistry and less recharge is deteriorating water quality. Higher rain recharge is also increasing NO_2^- pollution in Jehlam, Chakwal, and MB-Din (Fig. 2) as 0.3 correlation coefficient (Table 2) was found in whole of Punjab. Higher mean of

g

Fig. 2 (continued)

Table 1 Summary of groundwater quality variables of 46,457 samples at Punjab level

Statistical parameter	TDS	As	F ⁻	Fe	NO ₃ ⁻	NO ₂ ⁻	pH
Mean	862.67	12.83	0.74	0.13	9.93	0.82	7.59
Median	700.00	5.00	0.52	0.04	0.00	0.00	7.50
Mode	560.00	0.00	0.00	0.00	0.00	0.00	7.40
Standard deviation	715.07	25.39	1.99	0.35	26.14	19.74	0.54
Sample variance	511,324.27	644.43	3.96	0.12	683.21	389.79	0.29
Kurtosis	623.90	89.89	2023.42	4790.67	2061.17	20,742.12	17.17
Skewness	11.73	6.44	41.78	48.86	26.88	136.22	-0.90
Max	52,360.00	735.00	121.00	37.20	2215.00	3033.00	10.90
Min	50.00	0.00	0.00	0.00	0.00	0.00	0.09

Bahawalnagar or Bahawalpur might be due to stoppage of recharge from Rivers Ravi and Sutlej, intrusion of salty groundwater from Rajasthan [84, 85], industrial drain which stretches from Kasur along the Indian border up to the Arabian sea. Most districts of non-saline (mean data)

have hard rock, confined aquifer [47], continuous recharging from rain, less industrial density (Figs. 2 and 3 in supporting information) and less agriculture pollution as compared to classes 1 and 3 of mean data (Tables 3 and 4).

Table 2 Correlation of socioeconomic factors with water quality parameters

Dependent variable	TDS	As	F ⁻	Fe	NO ₃ ⁻	NO ₂ ⁻	pH
Rain(mm)	-0.28	-0.22	0.17	0.10	0.24	0.30	-0.27
Industrial density (#/km ²)	0.40	0.33	-0.02	0.00	0.31	-0.10	0.06
Tube well density (#/km ²)	-0.04	0.05	0.39	0.08	0.36	0.27	-0.37
Human population density (#/km ²)	0.19	0.38	0.04	0.00	0.19	-0.07	0.05
Animal population density (#/km ²)	0.24	0.31	-0.03	0.16	0.12	-0.11	-0.04
Fertilizer density (× 1000 ton/km ²)	0.53	0.40	0.18	0.31	0.06	-0.02	-0.04

Table 3 HCA-based class centroid for each variable

Class	TDS	As	F	Fe	NO ₃ ⁻	NO ₂ ⁻	pH
1	987.543	13.679	0.790	0.213	10.535	0.641	7.610
2	651.794	8.836	0.882	0.164	14.627	8.201	7.499
3	1358.873	11.787	0.873	0.143	25.218	0.663	7.982

Table 4 Distribution of Punjab districts into three classes determined through HCA

Class	District
1	Bahawalpur, Bahawalnagar, Khanewal, Lodhran, Multan, Muzafar Garh, Vehari, DG Khan, Lahore, Kasur, Pakpattan, Sahiwal, Jhang, Khushab, Gujranwala, Gujrat, Hafizabad
2	Attock, Mianwali, Bhakar, Layya, R-Y-Khan, Rajanpur, Rawalpindi, Chakwal, Jehlam, MB-Din, Sargodha, Chiniot, Sheikhupura, Nankana Sahib, Narowal, Sialkot, TT Singh
3	Faisalabad, Okara

The most polluted Faisalabad district has single unconfined aquifer with alluvial deposits [47]. It consists of sand, silt, silty clay, and cankers. Down to Okara, near Harappa, Bari Doab has sandy aquifer. Hard rock is not present in Bari Doab; rather, coarse sand is common [86]. In the Thal, Bari, and Rechna Doab, water level rose after Indus water irrigation canals system was introduced in 1912 and it contributed to increase in the level up to 1960; from 1960 onward, government decided to increase tube well irrigation because of higher crop intensity [86], but it leads to higher water TDS due to possible water mining pressure [87, 88]. Water table of lower part of Bari Doab has current depletion rate of 0.55 m in contrary to upper part (Balloki & Okara) that has stable water table due to lower Bari Doab canal (LBDC) & higher Rain [86]. Bari Doab has more

Fig. 3 Dendrogram shows three classes of groundwater: northwestern districts (green), central (pink), and southeastern districts (maroon)

Table 5 Eigenvalue, variability, and cumulative % of each extracted component through PCA

	F1	F2	F3	F4	F5
Eigenvalue	1.90	1.40	1.11	1.03	0.89
Variability (%)	30.21	23.12	20.25	17.14	6.21
Cumulative %	30.21	53.33	73.58	90.72	96.93

industries and less rain in lower part; that is why, water is more deteriorated in this region than northwest.

3.3 PCA

Principal component analysis (PCA) discovered 4 principal components based on Kaiser's criterion (Table 5). Only 4 components have eigenvalue greater than 1 and contribute 90.72% of cumulative % variability. Principal

component analysis found all ions positively correlated with TDS except NO_2^- (Table 6). Weak correlations values of TDS versus other pollutants suggest major contribution in TDS might be due to Na^+ , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , and Cl^- [60, 89, 90]; pesticides and dyes products in Faisalabad or meteoric conditions [91]. Angle between PCA variables shows (as shown by red dot in Fig. 4a) TDS and NO_2^- are negatively correlated as angle $\sim 180^\circ$ while As, NO_3^- , Fe, and TDS are positively correlated as angle $< 90^\circ$; Fe and NO_2^- are not correlated as angle $\sim 90^\circ$.

The first component (F1) with eigenvalue of 1.90 accounts for 30.21% of the total variability due to rain or water streams recharge. Positive loading of all ions and TDS in F1 (Table 7) shows same direction except NO_2^- [90]. All variables have lower values than TDS, showing TDS has more variability than As, Fe, NO_3^- in F1 direction. Districts with high rainfall, Indus River path, Mangla and Chasma Lake are present in left side (Fig. 4a) and bottom quadrants

Table 6 Pearson correlation coefficient determined through PCA

Variables	TDS	As	F ⁻	Fe	NO_3^-	NO_2^-	pH	Depth
TDS	1	0.26	0.06	0.24	0.11	-0.38	0.32	-0.276
As	0.26	1	-0.02	-0.01	0.14	-0.28	-0.15	-0.112
F	0.06	-0.02	1	-0.02	-0.14	-0.04	-0.00	-0.042
Fe	0.24	-0.01	-0.02	1	0.22	-0.01	-0.16	0.089
NO_3^-	0.11	0.14	-0.14	0.22	1	-0.21	-0.06	-0.037
NO_2^-	-0.38	-0.28	-0.04	-0.01	-0.21	1	-0.31	0.021
pH	0.32	-0.15	-0.00	-0.16	-0.06	-0.31	1	-0.046
Depth	-0.28	-0.11	-0.04	0.09	-0.04	0.02	-0.05	1

Fig. 4 Distribution of various districts based on their factor values. **a** Distribution based on water quality parameters (left); **b** distribution based on socioeconomic factors and rain (right)

Table 7 Factor loading after varimax rotation determined by PCA

	F1	F2	F3	F4
TDS	0.78	0.09	0.09	0.25
As	0.49	-0.31	0.48	-0.55
F	0.00	0.30	0.74	0.404
Fe	0.23	-0.61	-0.01	0.66
NO ₃ ⁻	0.39	-0.56	-0.33	-0.021
NO ₂ ⁻	-0.77	-0.17	0.00	0.17
pH	0.43	0.69	-0.40	0.146

(4b); same districts with less rain and less river recharge are located in right side (Fig. 4a) and top two quadrants (Fig. 4b).

F2 with eigenvalue of 1.40 has negative loading of Fe, As, NO₃⁻, and NO₂⁻, while it has positive loading of pH and F⁻ (Fig. 4a, Table 7). Fertilizer consumption is increased from one million ton to three million tons since 1980 to 2007 [11]; therefore, it is possible that F2 is related to pollution sources like industries, fertilizers, population, and maneuvers. It shows As, Fe, and NO₃⁻ (Fig. 4a) can be due to anthropogenic source, e.g., fertilizers, sewage, and other pollution sources [11]. F2 has major contribution from industrial activities as all industrial cities vary along vertical axis in Fig. 4a and b, as Faisalabad is at the top (Fig. 4a). Shallow hand pumps water has more nitrate contamination than deep boring; this is due to fertilizer seepage of NO₃⁻ and As [11]. Negative charge of NO₃⁻ and porous soil of Punjab lead to higher permeability to groundwater from agriculture source [77].

Samples in upper right quadrant (Fig. 4a) are enriched with TDS, F⁻ and pH; those in lower-right quadrant are enriched with NO₃⁻, Fe and As. Those in lower-left quadrant are enriched with NO₂⁻. Slight-saline to saline districts with worse quality appear in right quadrant (Fig. 4a) and severity increases to the extreme right (Fig. 4a). Faisalabad and Bahawalpur are at top right quadrant due to TDS, while Okara has significant TDS, As, Fe, and NO₃⁻ contribution. Districts with non-saline groundwater appear in left quadrant, while quality increases to the extreme left, except NO₂⁻ pollution that also increases in the extreme left (Fig. 4a). Higher NO₂⁻ in Jehlam & MB-Din might be due to water logging. Districts with medium level salinity and trace elements contamination (Chiniot, Sialkot, Hafizabad) fall in center of the line (Fig. 4a). Districts with higher pollutants in Fig. 4a are same with higher socioeconomic activities in top-right quadrant of Fig. 4b. Districts with less pollutants in left side of Fig. 4a are similar with higher rain in Fig. 4b (bottom-right).

F3 with eigenvalue 1.11 (Fig. 4a) has negative loading (Table 7) of pH and nitrate, while As and F⁻ have positive loading (Fig. 4 in supporting information). F3 has positive

loading of As and F⁻ which might be due to anthropogenic source (fertilizers contain F⁻ ~ 53–255 mg/Kg, As ~ 5–10 mg/Kg [28]. F4 with eigenvalue of 1.04 shows F⁻ and Fe also contribute to TDS from geological origin [2, 10]. F4 shows TDS, F, and Fe have same source and As may be due to other sources [12, 16].

A study in the Tharparkar reported TDS 937–7690 mg/L, while Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe were found to be 166–2180, 8.16–22.3, 26.9–482, 48.9–207, and 0.109–0.327 mg/L, respectively. Brahman argued high As and F⁻ may be due to complex geochemical factors, including geological factors, climatic effect and agriculture pollution using principal component analysis [58]. Arsenic and fluoride are contributed by pesticide, fertilizers, hydrofluorocarbon, and water abstraction [18, 21]. Hydroxyapatite mineral releases As in high-alkaline water, while F⁻ is enriched in alkaline environment, minerals weathering, fluorite dissolution, dolomite dissolution, and arid conditions [11, 13]. Urea fertilizer contributes to NO₃⁻ and NO₂⁻ pollution in addition to animal waste [28]. Tube well abstraction also increases TDS levels in addition to sewage waste [28, 30]. Most vulnerable Bari Doab districts groundwater recharge is severally reduced, as Ravi and Sutlej Rivers have been dried [12]. Published literature and current study proves pollution is enhanced by socioeconomic sources.

3.4 Spatial variation in TDS

Current studies found 8 districts out of 36 districts have mean TDS > 1000 mg/L (Fig. 2g, Tables 1, 2, and 3 in supporting information). These are Faisalabad (1405.76 mg/L), Gujranwala (1063.96), Okara (1311.99 mg/L), Sahiwal (1188.48 mg/L), Kasur (1041.39 mg/L), Bahawalpur (1105.38 mg/L), Khushab (1112.37 mg/L), and Gujrat (1011.70 mg/L). Four out of 8 districts are industrial cities (Faisalabad, Gujranwala, Kasur, and Gujrat), while Okara, Sahiwal, Bahawalpur are agriculture districts, and Khushab is an agriculture and mining hub (Fig. 2 in supporting information).

Districts with mean TDS ~ 751–1000 mg/L are considered at threat level because majority samples of these districts have TDS > 1000 mg/L. Eight districts of this group fall in 900–1000 mg/L range. These are Lahore (948.65 mg/L), Hafizabad (946.50 mg/L), Bahawalnagar (920 mg/L), Pakpattan (969.84 mg/L), Vehari (972.86 mg/L), Khanewal (909.58 mg/L), DG Khan (922.34 mg/L), Multan (929.34 mg/L), and Muzafar Garh (994.74 mg/L), while Lodhran (874.85 mg/L), Jhang (876.27 mg/L), TT Singh (811.56 mg/L), and Rajanpur (782.06 mg/L) also lie in slight saline range (751–1000 mg/L).

The districts which have TDS 501–750 mg/L are relatively safe; these are Attock (656.45 mg/L), Rawalpindi (614.74 mg/L), Chiniot (655.51 mg/L), Mianwali

Fig. 5 Two-hump TDS distribution shows contribution of two different types of groundwater in Faisalabad

(682.90 mg/L), Sargodha (644.55 mg/L), and Nankana Sahib (711.64 mg/L), Sheikhpura (720.02 mg/L), Sialkot (734.56 mg/L), Narowal (738.89 mg/L), and Bhakar (541.91 mg/L). These districts have high rainfall or Indus/Chenab/Jhelam recharge and less industry. The completely safe districts have ≤ 500 mg/L; these are Chakwal (466.18 mg/L), Jhelam (495.83 mg/L), and MB-Din (500.37 mg/L). Complete safe districts are part of Pothwar confined aquifer, high rainfall, Mangla lake, and Jhelam River recharge.

Faisalabad mode and median TDS are 2439 mg/L and 1179.50 mg/L, while mean value is 1405.76 mg/L. These data prove there is no particular site in Faisalabad which increases the mean value; rather, most of the sites have higher TDS and it falls into severe saline due to mode value. TDS distribution shows two humps (Fig. 5), the median of first hump is at 950 mg/L, while second hump median is formed at 2150 mg/L. These two humps are representative of rural and urban groundwater quality. The higher TDS hump has industrial, urbanization, and sewage contribution; however, 950 mg/L hump has agriculture pollution and evaporation base seepage.

Okara district mode and median TDS are 1435 mg/L and 980 mg/L, respectively, while it has single hump histogram. Histogram shows Okara does not have any urban/rural significant difference and higher TDS is due to agriculture industry. Okara lies in middle of the Bari Doab, and it is agriculture district and has the highest number of tube wells [92]. The next geographical neighbor of Okara is Sahiwal, and it follows similar trend to Okara in all aspects as its mean, median, and mode are 1188.48, 1010.50, and 924.00 mg/L, respectively with single hump

histogram. The median of (Rural) Faisalabad, Okara, and Sahiwal is 950 mg/L, 980 mg/L, and 1010.5 mg/L, respectively. The median values are very close, and these districts are geographically connected to each other; it is possible agriculture activities are dominating reasons of TDS, while stoppage of fresh water recharge from two rivers due to Indus water treaty is setting new baseline of groundwater quality. Agriculture streams in Punjab were cemented during 2002–2008 which might have decreased water recharge that can be one of the reasons behind higher TDS at micro-level; however, proper investigation is required. The eastern neighbor of Okara is Kasur whose mean, median, and mode TDS are 1041.39, 815.50, and 700 mg/L, respectively. Median and mode of Kasur are less than Okara; therefore, it is expected that certain locations are polluted and mean value is increased; however, most sites are safe (mode ~ 700 mg/L). Due to small tube wells, BRB and UC link-canals, recharge is enough and TDS is < 1000 mg/L. Pakpattan has mode value of TDS ~ 1177 mg/L, while its median and mean are 885 and 969.84 mg/L, while Sahiwal and Faisalabad neighboring TT Singh mode is 1019 mg/L, higher than WHO, while its mean and median are 811.56 and 574 mg/L. Gujranwala, Faisalabad, Okara, Pakpattan, Layya, and TT Singh follow trend of Mode $>$ Mean $>$ Median.

Most of the south Punjab districts (Sahiwal, Bahawalpur, Bahawalnagar, DG-Khan, Khanewal, Multan, Lodhran, Muzaffargarh, Rajanpur), Kasur, Nankana Sahib, Sialkot, Mianwali, follow trend of mean $>$ median $>$ mode. Skewness of all districts is positive (positively skewed, skewness ~ 1 –1988) which shows uneven distribution due to contaminations at higher side.

Indus water passes from Attock, Mianwali, Bhakar, Muzafar Garh, and R. Y. Khan; the mean TDS in most of the districts is below 700 except Muzafar Garh (mean TDS ~ 994.71); mode of Muzafar Garh is also 450 mg/L; hence, the data show proper recharge of groundwater in these districts. TDS of current study shares many common features with already published data [10] which proves the validity of current findings. The remaining districts: Jhang, Vehari, R-Y-Khan follow Mean $>$ Mode $>$ Median.

Based on nonlinear predictive modeling, Eq. (2) was derived which predicts TDS for given values of trace pollutants. It is nonlinear multiple regression model and explains 70% variance in TDS at Punjab provincial level under current recharge conditions.

$$\begin{aligned} \text{TDS} = & 403472 + 13.59\text{As} + 552.34\text{F}^{-1} + 101.66\text{Fe} - 44.79\text{NO}_3^{-1} - 22.49\text{NO}_2^{-1} - 15305\text{pH} \\ & + 0.42\text{As}^2 - 928.56(\text{F}^{-1})^2 + 640.58\text{Fe}^2 + 2.12(\text{NO}_3^{-1})^2 + 0.64(\text{NO}_2^{-1})^2 + 19607\text{pH}^2 \\ & - 0.014\text{As}^3 + 553.32\text{F}^3 - 530.29\text{Fe}^3 - 0.02(\text{NO}_3^{-1})^3 - 0.01(\text{NO}_2^{-1})^3 - 826\text{pH}^3 \end{aligned} \quad (2)$$

3.5 Water quality model with respect to socioeconomic parameters

Rain, river, and canal recharge improve water quality, while industrial effluents, water abstraction, agriculture fertilizers, pesticides, animal density, human population, and urban sewage dumps deteriorate the water quality. Soil type can affect groundwater quality. Correlation between TDS and socioeconomic factors shows influence of each factor on groundwater quality (Table 2).

3.5.1 Soil, agriculture, industrial activities

Punjab is divided into five different soil types (Table 8), Sind Sagar Doab has two different types of soil, and right bank of Indus after Panjnad is different. Jech, Rechna, and Bari Doab have Loamy, clayey, non-calcareous soil, while left bank of Sutlej also has sandy soil. Water mining in shallow water tables and permeable soil induces groundwater recharge [2, 10] by producing significant vertical head [93]. Therefore, it is also expected that soil combined with tube well abstraction in center and southeast Punjab has severally affected shallow groundwater. In addition, agriculture activities and pollutants are higher in southeast and center Punjab (Fig. 4). Correlation of 0.40 was found between TDS and industries while 0.53 between TDS and fertilizes. Industry is also higher in center and southeast Punjab (Fig. 2 in supporting information) and contributes to more contaminations. Indus water canal Irrigation system was designed for cropping intensity of 67% which has steadily increased to 160% at present level [86]. Increase of groundwater irrigation leaves salt deposit due to high temperature climate in the center and southeast Punjab. Increase in temperature increases

evaporation in lower Bari Doab & south Punjab districts [94], and later irrigation increases seepage to groundwater [2, 10].

3.5.2 Seepage, recharge, and rain

Rain recharge is dominated if rainfall > 1000 mm; if rainfall is ~ 500–1000 mm, recharge is likely to be met by canal leakage and rainfall. If rainfall occurs < 500 mm, recharge is dominated by irrigation returns and canal leakage [2]. Rainfall decreases gradually north to south, as Lahore, Faisalabad, and Multan have 710, 370, and 200 mm of rain, respectively (Fig. 3 in supporting information), while TDS is inversely correlated with rain having – 0.28 of correlation coefficient (Table 2). Average rainfall in north Punjab (Jehlam, Sialkot, Narowal, and Lahore) is 900–1000 mm; moreover, link canals also add to recharge. South Punjab (Multan, Lodhran, Muzafar Garh, and surrounding) has annual rainfall ~ 150–200 mm. Therefore, it is concluded that center and south Punjab [95] recharge is only through link canals and rivers. Two rivers have (Ravi and Sutlej) have dried, and therefore, only recharge is due to small leftover water of Trimmu and Indus. Muzafar Garh may have salinity of shallow water due to overcharging from Indus, Taunsa–Panjnad link canal, and Jehlam–Chenab–Ravi–Sutlej (JCRS) combined stream. North side has generally rain recharge, while west side is recharged by Indus.

Influence of socioeconomic factors and rain was modeled for TDS as these affect groundwater quality. A nonlinear model explains 57% variance in TDS using rain, industrial, tube wells, human population, animal population, and fertilizer density as independent variables. Remaining variance might be due to pesticides, geological factors or other socioeconomic activities. Equation (3) can predict

Table 8 Types and characteristics of Punjab soil [96]

Regions	Districts	Soil composition	Activity
Pothohar	Rawalpindi, Jehlam, Attock, Chakwal	Loam, loess and residual, shallow loamy gravelly, rocks of plateau and mountain. Deep water	Arid agriculture
Thal desert	Part of Khushab, Bhakkar, Layya, Muzafar Garh, and Mianwali	Sandy	Arid & flood agriculture
Fertile Indus plain	Central, south, northeast Punjab	Loamy, clayey of old flood plain, clayey non-calcareous of old terrace	Flood agriculture
Plain to plateau	Rajanpur, DG-Khan	Sandy loamy silt of piedmont plains, shallow loamy gravelly sol, rock of plateau and mountain	Flood agriculture
Cholistan desert	Bahawalpur, Part of R-Y-Khan and Bahawalnagar	Sandy	Arid & flood agriculture

any change in TDS due to all possible factors until the river recharge remains at current level.

$$\begin{aligned} \text{TDS} = & 916 + 0.42R - 2390I + 22T + 0.54P \\ & - 5266A + 37035F - 2.6 \times 10^{-4}R^2 + 13432I^2 \\ & - 3.58T^2 - 3.5 \times 10^{-4}P^2 + 19027A^2 - 1987977F^2 \\ & - 4.37e^{-7}R^3 - 1.61 \times 10^4I^3 + 0.1T^3 + 1.24e^{-7}P^3 \\ & - 22062A^3 + 3019e^4F^3 \end{aligned} \quad (3)$$

where R =Rain, I =industrial density, T =tube well density, P =population density, A =animal density, F =fertilizer sale density (fertilizer sale per square kilometer of the area).

4 Conclusions

Various parameters exceed WHO safe limits, as they were found to be 26% of TDS, 8.07% of As, 10.63% of F^- , 1% of Fe, 1.33% of NO_3^- , and 0.92% of NO_2^- . Punjab was dissected into northwest and southeast based on its groundwater quality. Northwest has better quality due to rain and river recharge, and southeast (along India border) has deteriorated quality due to less rain, less river recharge, and higher socioeconomic activities. Faisalabad and Okara have worst salinity in the region. PCA suggested agriculture and industry are dominantly increasing TDS, while river and rain recharge are decreasing TDS. Therefore, it is concluded that Indus water treaty has changed the water quality in addition to industrialization, agriculture, and population, farming and rain. The following points can be concluded from the current study:

- Geology of (Indian and Pakistani) Punjab is similar, and deterioration in groundwater quality of one can affect the neighboring Punjab.
- Water quality can be improved by careful planning crops intensity, controlling water abstraction, flood irrigation, industrial pollution, and fertilizer consumption.
- Canal water should be provided for agriculture, and north–south canals should be constructed for recharge.
- Canals should be belt from Trimmu passing from Khanewal, Lodhran, Multan, Vehari, and Bahawalpur. Canal should be belt at Kalabagh, passing from Khushab, Jhang & TT-Singh. A canal should be belt from Chenab to Ravi, passing from Faisalabad, Sahiwal, Vehari, and Pakpattan ending at Bahawalnagar. Water should be managed from other link canals and rivers for new canals.
- Indus water treaty should be re-negotiated between India and Pakistan to increase water in Ravi and Sutlej for conservation of the environment.

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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