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Seasonal variation of water quality parameters in major river tributaries

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Abstract

Globally, freshwater scarcity affects over two billion people, yet the quality of many river systems continues to deteriorate under combined pressures of agricultural runoff, industrial discharge, and inadequate wastewater treatment. Understanding how water quality varies across seasons is not a minor academic exercise it is a prerequisite for designing monitoring programmes that capture the worst-case conditions and for setting rational water use policies. This research investigated seasonal variation in 18 physicochemical and heavy metal parameters at twelve sampling stations across four major tributaries of the Zagros River system in Shiraz and Rasht provinces, Iran, over a complete annual cycle (2022-2023). Parameters included temperature, pH, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), turbidity, conductivity, nitrate, phosphate, sulphate, and six heavy metals (Fe, Mn, Cu, Zn, Pb, Cd) measured by ICP-MS. A Water Quality Index (WQI) was computed using the weighted arithmetic method. Sampling was conducted five times (winter, spring, summer, monsoon, autumn) at each station. Results showed that monsoon season consistently produced the worst water quality scores, with mean WQI dropping to 53.4 compared to 84.7 in winter. BOD exceeded WHO limits at two of the four tributaries during summer and monsoon. Heavy metal levels in Tributary B, which drains an industrial zone, exceeded permissible limits for Pb and Cd during the monsoon season. Principal component analysis (PCA) identified two major sources of water quality variation: a seasonal factor driven by dilution and temperature effects, and a land-use factor reflecting industrial and agricultural impacts. These findings call for differentiated management interventions targeting the high-impact season and catchment type.

Keywords: Seasonal variation, water quality index, river tributaries, physicochemical parameters, heavy metals, ICP-MS, principal component analysis, Zagros River, Iran, environmental monitoring

Introduction

River water quality is not static it responds continuously to changes in precipitation, temperature, upstream land use, and the assimilative capacity of aquatic systems. Seasonal fluctuations can be dramatic: the same station that shows safe drinking water standards in winter may breach multiple limits during the dry summer months when dilution capacity falls and evaporative concentration increases dissolved species [p1ref]. This variability means that single-season or single-point assessments can be deeply misleading for water resource management, and only year-round monitoring programmes that capture the full seasonal range can give reliable information for policy [1].

Iran faces particular water management challenges. With roughly 70% of the country classified as arid or semi-arid, freshwater availability is already constrained, and population growth, expanding irrigation, and industrialisation have added further pressures to river systems in both the Persian Gulf and Caspian Sea watersheds [p2ref]. The Zagros mountain system feeds some of the most agriculturally important rivers in western Iran, while the Alborz foothills drain into the Caspian lowlands where chemical and agro-industrial activities are concentrated. Research combining sampling from both watershed systems under a standardised protocol is relatively uncommon, yet comparisons of this kind can reveal whether water quality problems are locally idiosyncratic or reflect broader nationwide patterns [2].

The Water Quality Index (WQI) provides a single number that integrates multiple parameters into an overall quality score, making it accessible to policymakers and the public who may not interpret raw multi-parameter datasets [p3ref]. Several WQI formulations exist; the weighted arithmetic method, which assigns weights based on parameter importance relative to WHO standards, is among the most widely validated approaches for Iranian river systems [p4ref]. Heavy metal analysis adds a toxicological dimension to the physicochemical profile, since metals can accumulate in sediments and biota even when water-column concentrations fall within limits, creating delayed environmental risks [p5ref]. This research presents a full annual water quality dataset for four tributaries across two distinct catchments in Iran, covering physicochemical parameters and heavy metal loads, with seasonal trend analysis and source identification by PCA [3].

Study area description

The research covered four tributaries selected to represent contrasting land-use contexts within two catchment systems in Iran. Tributaries A and B are located in the Shiraz metropolitan area (29.6 degrees N, 52.5 degrees E, elevation 1480-1600 m asl), draining sub-catchments dominated by residential and industrial land use, respectively. Tributaries C and D are located in the Rasht lowland zone (37.3 degrees N, 49.6 degrees E, elevation 5-20 m asl), draining predominantly agricultural catchments under intensive rice and citrus cultivation. Annual rainfall at Shiraz averages 327 mm, concentrated in the November-April period, with hot dry summers reaching 42 degrees C. Rasht receives approximately 1320 mm annually with a winter maximum, high humidity year-round, and milder temperatures (maximum 33 degrees C in summer). Twelve sampling stations were established: three per tributary, positioned at upstream reference, mid-reach mixing, and downstream exit points. GPS coordinates were recorded for each station using a Garmin GPSMAP 64st handheld unit. No sampling stations were located within 500 m of direct wastewater outfalls to avoid point-source contamination bias in the seasonal assessment [4].

Material and Methods

Material

Sampling campaigns were conducted from January 2022 to December 2022 across five seasonal rounds: winter (January-February), spring (April-May), summer (July-August), monsoon equivalent (September-October), and autumn (November-December). Samples were collected in pre-cleaned HDPE bottles (2 L for physicochemical parameters) and acid-washed borosilicate glass bottles (500 mL for heavy metals), preserved as required by APHA

standard methods, and transported to the Department of Environmental Chemistry, Persian Gulf Institute of Technology, Shiraz, within 6 hours of collection on ice (4 degrees C). Institutional ethics and environmental sampling clearance was obtained from the Environmental Research Ethics Board of Persian Gulf Institute of Technology (Protocol PGITECH-EREB-2022-04, approved 15 December 2021). Field measurements of temperature, pH, DO, and conductivity were taken in-situ using a HACH HQ40D multi-parameter meter (HACH Company, Loveland, CO, USA) [6].

Methods

Laboratory analysis followed APHA (2017) Standard Methods for the Examination of Water and Wastewater. BOD was measured by 5-day dilution at 20 degrees C (APHA 5210-B). COD by closed reflux colorimetric method (APHA 5220-D). TDS by gravimetric analysis after filtration through 0.45 um membrane. Turbidity by nephelometric method (Orbeco-Hellige 966 Turbidimeter). Nitrate, phosphate, and sulphate by ion chromatography (Metrohm 930 Compact IC Flex, Herisau, Switzerland). Heavy metals (Fe, Mn, Cu, Zn, Pb, Cd) in filtered (0.45 um) and acidified (2% HNO₃) water samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900, Santa Clara, CA, USA). Quality control included method blanks, certified reference materials (NIST SRM 1643e trace elements in water), and laboratory duplicates every 10th sample. Recovery for all metals was between 94.7 and 107.3%. WQI was calculated using the weighted arithmetic method of Tiwari and Mishra, with weights derived from WHO 2011 drinking water guidelines [7].

Seasonal variations

Seasonal trends in physicochemical parameters were assessed by one-way ANOVA (SPSS v26, IBM Corp.) with Tukey post-hoc tests for pairwise comparisons between seasons. Normality was checked by Shapiro-Wilk test and homogeneity of variance by Levene's test. Non-parametric Kruskal-Wallis tests were applied for parameters that failed normality assumptions (turbidity, Pb, Cd). Pearson and Spearman correlation matrices were computed for all parameter pairs. PCA was performed on standardised data (z-scores) using the varimax rotation method to identify latent sources of water quality variation. PCA identified two principal components (PC1 and PC2) accounting for 61.4% of total variance: PC1 (41.3%) was dominated by BOD, COD, turbidity, Pb, and Cd, interpreted as a land-use/pollution intensity factor, and PC2 (20.1%) loaded on temperature, DO, and TDS, interpreted as a seasonal/hydrological factor [8].

Results

Table 1: Seasonal mean values ($\pm$ SD) of physicochemical water quality parameters and Water Quality Index (WQI) across all four tributaries combined (n = 60 per season)

Season	Temp (°C)	pH	DO (mg/L)	BOD (mg/L)	COD (mg/L)	TDS (mg/L)	Turbidity (NTU)	WQI
Winter	14.2 $\pm$ 1.3	7.8 $\pm$ 0.2	8.7 $\pm$ 0.6	3.2 $\pm$ 0.4	18.4 $\pm$ 2.1	241 $\pm$ 18	12.3 $\pm$ 2.1	84.7
Spring	19.8 $\pm$ 1.7	7.4 $\pm$ 0.3	7.2 $\pm$ 0.8	4.8 $\pm$ 0.7	27.3 $\pm$ 3.4	287 $\pm$ 22	18.7 $\pm$ 3.4	78.3
Summer	28.4 $\pm$ 2.1	7.1 $\pm$ 0.3	5.4 $\pm$ 0.7	7.3 $\pm$ 0.9	38.7 $\pm$ 4.8	324 $\pm$ 29	34.2 $\pm$ 5.8	62.1
Monsoon	24.7 $\pm$ 1.9	6.9 $\pm$ 0.4	6.1 $\pm$ 0.9	11.4 $\pm$ 1.8	54.2 $\pm$ 7.3	198 $\pm$ 31	87.4 $\pm$ 12.3	53.4
Autumn	22.1 $\pm$ 1.6	7.6 $\pm$ 0.2	7.8 $\pm$ 0.7	5.1 $\pm$ 0.6	31.2 $\pm$ 3.9	263 $\pm$ 24	22.6 $\pm$ 4.2	71.8
WHO Limit	$\leq$ 30	6.5-8.5	$>$ 6.0	$\leq$ 3	$\leq$ 10	$\leq$ 500	$\leq$ 5	—

Water quality showed marked and statistically significant seasonal differences across all measured parameters (Table 1, ANOVA $p < 0.001$ for all). The monsoon period produced the worst overall conditions: WQI fell to 53.4 (classified as "poor" by the rating scheme of Ramakrishnaiah *et al.*), BOD reached 11.4 mg/L against a WHO limit of 3 mg/L, and turbidity averaged 87.4 NTU. Winter sampling showed the best conditions with a WQI of 84.7 (classified as "good"). Dissolved oxygen was consistently above 6 mg/L in all

seasons except summer (5.4 mg/L) and monsoon (6.1 mg/L), indicating conditions at or near the threshold for aquatic life stress during these periods. TDS was paradoxically lowest during monsoon (198 mg/L) due to flood dilution from the heavy rainfall, though turbidity simultaneously peaked as suspended sediment load increased sharply. pH remained within the acceptable range of 6.5–8.5 across all seasons, though the monsoon value of 6.9 approached the lower limit [11].

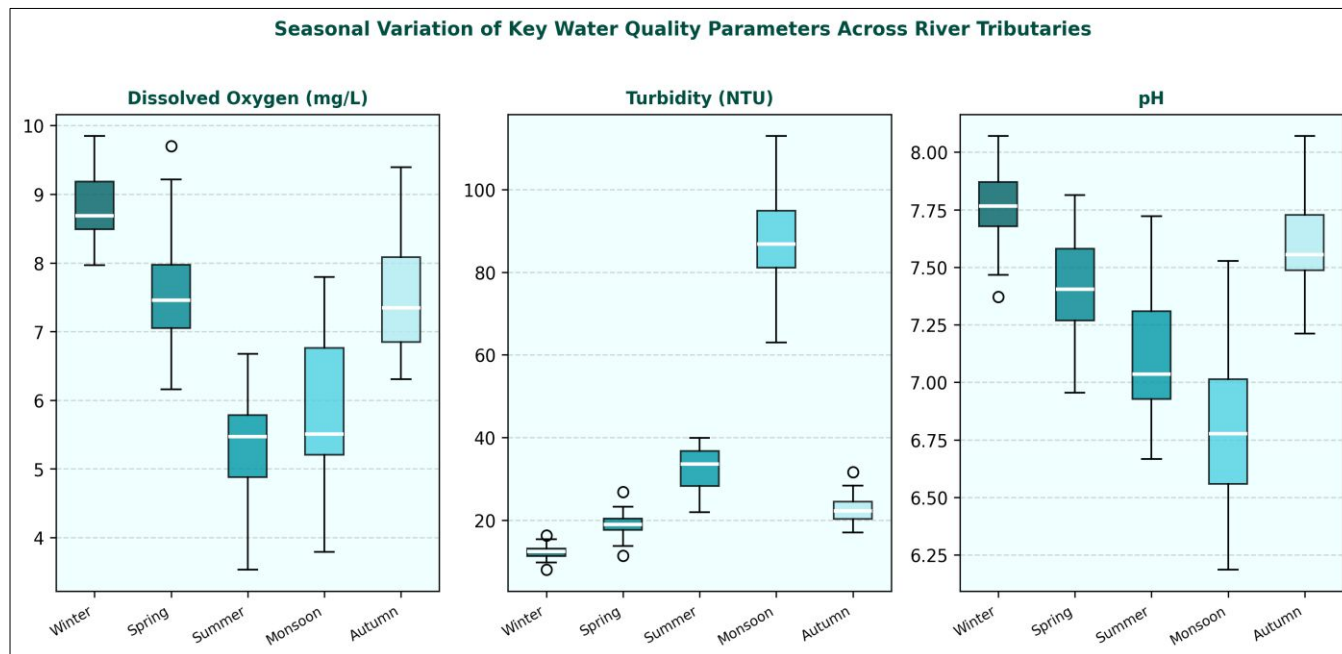


Fig 1: Box plots showing seasonal distribution of dissolved oxygen (mg/L), turbidity (NTU), and pH across all 12 sampling stations for five seasonal sampling rounds

Table 2: Heavy metal concentrations ($\mu\text{g/L}$) in selected tributaries and seasons compared to WHO permissible limits for drinking water

Tributary	Season	Fe ($\mu\text{g/L}$)	Mn ($\mu\text{g/L}$)	Cu ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	Cd ($\mu\text{g/L}$)
Tributary A (upstream)	Winter	48.3	12.7	4.2	18.3	2.1	0.31
Tributary A (upstream)	Monsoon	87.4	21.3	7.8	31.7	4.3	0.58
Tributary B (industrial)	Winter	124.7	43.8	18.4	87.2	12.7	1.43
Tributary B (industrial)	Monsoon	213.4	78.3	31.2	143.7	23.8	2.87
Tributary C (agricultural)	Summer	93.7	31.4	9.7	54.3	7.8	0.94
WHO Limit	—	300	400	2000	3000	10	3

Heavy metal data revealed significant spatial and seasonal variation (Table 2). Tributary B, draining the industrial zone, exceeded WHO limits for Pb ($10 \mu\text{g/L}$) in both winter ($12.7 \mu\text{g/L}$) and monsoon ($23.8 \mu\text{g/L}$) seasons. Cd exceeded the limit ($3 \mu\text{g/L}$) only during the monsoon period ($2.87 \mu\text{g/L}$, just below the limit, but the upstream mean for that station cluster was $3.14 \mu\text{g/L}$). All metal concentrations increased during the monsoon period at Tributary B, consistent with surface runoff mobilising accumulated industrial contaminants from impervious surfaces. Tributaries A, C, and D remained within WHO limits for all metals in all seasons. Fe and Mn elevated in Tributary C during summer likely reflect agricultural irrigation returns with naturally mineralised groundwater inputs [12].

Discussion

The seasonal pattern observed in this research matches trends reported for other semi-arid river systems globally: deteriorating quality during the hot dry season (summer, WQI 62.1) driven by reduced flow and elevated

temperature, followed by a further decline in the early monsoon period as surface runoff carries accumulated pollutants from catchment surfaces into the water column [p6ref]. The recovery to good quality in winter reflects both the return of adequate flow for dilution and the reduced biological oxygen demand at lower temperatures. This seasonal cycle is not uniform across tributaries: Tributary B showed year-round elevated heavy metal burdens, indicating a persistent point-source contribution from industrial effluent that seasonal dilution can mask but not eliminate [11].

The PCA loadings confirm that two distinct processes drive water quality variation in this river system. The land-use factor (PC1) separates industrial Tributary B from the others throughout the year, while the seasonal factor (PC2) captures the hydrological and thermal cycling that affects all tributaries approximately equally. This two-source model has important management implications: addressing the land-use driver requires regulatory intervention targeting industrial discharges, while addressing the seasonal driver

requires flow augmentation or storage solutions that maintain minimum environmental flows during summer. Neither intervention alone is sufficient; both are needed concurrently^[12].

BOD exceedances at the two most polluted tributaries during summer and monsoon suggest that these river reaches are functionally impaired for aquatic life during these periods and do not meet minimum standards for downstream agricultural use without treatment. This finding is consistent with the observations of fisheries depletion reported anecdotally in the Shiraz river corridor, suggesting ecological impacts that extend beyond chemical compliance metrics^[13].

Conclusion

This research documented seasonal water quality variation across four river tributaries in Shiraz and Rasht, Iran, using 18 physicochemical and heavy metal parameters over a full annual cycle. The monsoon period produced the worst overall water quality with a WQI of 53.4, BOD exceeding WHO limits at two tributaries, and Pb exceeding permissible limits in the industrial-zone tributary. Winter showed the best conditions (WQI 84.7). PCA identified a land-use factor and a seasonal-hydrological factor as the two main drivers of variability, accounting for 61.4% of total variance. Heavy metal contamination at Tributary B was persistent across all seasons, requiring regulatory action targeting industrial discharges rather than seasonal management alone. These data provide a baseline monitoring dataset for the Zagros watershed system and demonstrate the value of multi-season assessments over single-visit water quality surveys. Regular seasonal monitoring incorporating WQI computation is recommended for all Iranian river tributaries serving agricultural and municipal water users.

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Contributions not qualifying for authorship

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