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Original Research

Reservoir Water Quality Assessment Based on Chemical Parameters and the Chlorophyll Dynamics in Relation to Nutrient Regime

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Abstract

Deteriorating water quality has become a global concern. Chungju Reservoir is the largest reservoir in South Korea. Here we describe the long-term spatiotemporal variabilities and prevailing trends in physicochemical and nutrient contributing factors using datasets of 1992-2016. Seasonal, annual, multivariate analytical techniques, and water pollution index (WPI) investigations revealed monsoon rainfall events as major influential element in fluctuating water quality. Total nitrogen (TN) and total phosphorus (TP) concentration was largely affected by the intensity of monsoon rainfall along the longitudinal gradient. Seasonal and inter-annual analyses indicated the reservoir system as being N-rich and strongly P-limited. They also indicated progressive escalation of pH, chemical oxygen demand (COD), TN, and TP – clarifying greater industrial and agricultural runoff. The transition zone *(Tz)* was crucial for leaching of suspended solids pointing toward an imminent siltation problem. Mann Kendal test confirmed a significantly increasing trend in pH, COD, TN, TP, and ammonium. Principal component analysis disclosed that water quality deterioration cannot be ascribed to a single point source but instead diffused sources. The trophic state index exhibited deviation from larger particles to severe zooplankton grazing as an explicit sign of oligo-mesotrophic state, leading to increased Secchi disk depth. WPI categorize the chemical health status as 'good.' Overall, it could be inferred that water quality was good but may face an impending degradation plus increasing nutrients and chemical loads.

Keywords: reservoir, chemical health, monsoon rainfall, water quality, zooplankton grazing, trophic state

Introduction

During the past few decades, freshwater resources are subjugated to increasing anthropogenic activities such as the construction of reservoirs for accruing the benefits of power generation, municipal water supply for drinking and household, transportation, flood control, recreation, agriculture, fishing [1], aesthetics, raising aquatic animals, and so on. Due to natural flow manipulations coupled with intensive rainfall [2], degradation of physiochemical water quality is very recognizable [3], besides trophic disarrays such as oligotrophy due to higher water retention time and

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depletion of initially higher allochthonous nutrient contributing factors [4]. Therefore, dams and reservoirs tenaciously or inadvertently alter the downstream water quality.

Water quality is assumed as the mainstay of public interest for monitoring disease and the state of healthiness in humans and aquatic organisms [5]. Freshwater quality is reportedly deteriorating because of rapid industrialization, expanding populations, and globally increasing pressure reinforced by poor management that ultimately has led to severe environmental degradation [6-7]. Water quality status is dynamic in nature and is normally estimated by approximation, deviation, or degradation of physicochemical parameters [8], which are mainly based on factor concentrations, e.g., phosphorus and nitrogen are essential within optimal ranges but become detrimentally noxious after deviation from favorable levels. Such alterations can be used for decision-making about targeted water use, for instance drinking, industrial, agricultural, and so on. Some water quality factors (e.g., phosphorus (P) and nitrogen (N)) respond promptly to environmental changes, whereas some (e.g., salinity) can take decades [9-10].

Eutrophication in lakes and reservoirs is rapidly increasing due to excessive discharge of nutrient-rich effluents originating from industry and agriculture in basin areas [11-12]. Primary production in terms of Chl-a production is a commonly used surrogate of eutrophication that is mainly based on phosphorus and nitrogen availability [13], and Carlson [14] has developed the trophic state index (TSI) for the assessment of eutrophication that is primarily based on Chl-a level in a water body. Numerous researchers have reported dealing mainly with eutrophication issues from the USA [15], Spain [16], Canada [17], China [12], South Korea [2], New Zeeland [18], Finland [19], and Brazil [20].

Chl-a has shown a positive linear relationship with total phosphorus levels in case of phosphorus-limited water bodies, and with total nitrogen (TN) in case of nitrogen-limited aquatic systems [19, 21]. Additionally, Chl-a is also closely dependent on Secchi dish depth (SDD), which is used as a measure of light availability in the water column. Interestingly, this paradigm, however, is continuously shifting due to monsoon rainfall in Asian lentic water bodies [2, 22]. Whatever the case, higher loadings of nutrients and organic matter may have a serious effect on Chl-a production as well as the biotic communities [23-24]. Therefore, nutrient contributing factors (N, P) and organic matter loads are decisively involved in concocting reservoir water quality. Furthermore, N:P mass ratios are broadly considered as a key factor for trophic state diagnosis as well as an indication of nutrient limitation [25-26]. If the N:P ratio is higher (>17), it points towards phosphorus limitation, but if it is low (<4), it indicates nitrogen limitation [27].

Multivariate analytical methods are frequently used for better understanding of water quality as well as the ecological health diagnosis of underground, lentic, and lotic waters. Such techniques help interpret the multifaceted data matrices in an easier and more comprehensive manner by allowing the identification of potential sources/factors than can be held responsible for watershed impact as well as present valuable means for trustworthy water resource management and solutions to pollution [28]. Principal component analysis (PCA), cluster analysis (CA), discriminate analysis (DA), and factor analysis (FA) are reportedly used in the scientific literature because of their ability to treat larger datasets of temporal and spatial parameters obtained from various study sites [5, 29-35]. PCA and CA have proven to be very important statistical tools for determining underlying relationships among various physicochemical parameters, pollutant source identification, and grouping sites or parameters into similar clusters for better understanding [5, 28, 31].

Chungju is an exoreic reservoir in in the northeastern South Korea and is famous for being the country's largest watershed area waterbody as well as having the second largest water storage capacity. This multipurpose manmade reservoir is predominantly dedicated to domestic water supply and flood control as well as hydroelectric power generation [36]. It is described by the titanic depth and lengthier water residence time during flood seasons and discharging water during dry periods. Owing to longer water retention time, more depth and larger surface area, Chungju is categorized more as a lake-type reservoir despite its riverlike embankments as well as long riverine zone. One of the important functions the reservoir plays is for discharging sustained water flows for significant environmental flow during the drought season for downstream water quality improvement in the river, reduced pollutant effects, and enhanced scenic amenities.

Given the grander importance of Chungju Reservoir as the hot spot of domestic water supply, hydroelectric power resource, a recreational point, and the largest waterbody of South Korea, this study was planned to assess: 1) the water quality status similarities and differences at the sampling stations, 2) seasonal and annual trends among the physiochemical quality parameters, 3) inflow and discharge dynamics, 4) nutrient and Chl-a interactions, 5) revealing the existing and future trends, and 6) the trophic status evaluation of Chungju reservoir.

Materials and Methods

Watershed and Study Area

Chungju is the largest concrete gravity dam (CGD) constructed during 1978-85 in South Korea upstream of the southern Han River system. The coordinates are 37°00′22″N 127°59′33″E. The layout of the reservoir, study sites, and zones are shown in Fig. 1. Salient hydrological features and dimensions are given in Table 1. During this study, three sampling stations were selected to investigate the longitudinal gradients of the

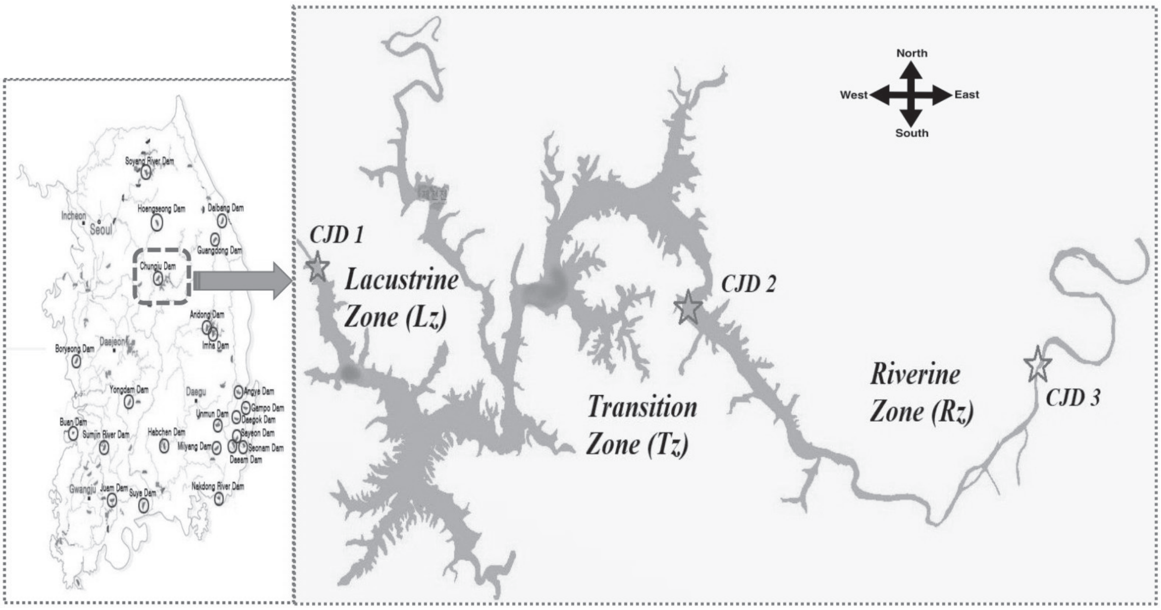

Fig. 1. The layout of Chungju dam showing its three different zones as well as the study sites.

Table 1. Salient geographic and limnological characteristics of Chungju Dam.

Hydrological and dimensional attributes	Characteristics
Construction period	1978-1985
Dam type	Concrete gravity dam (C.G.D.)
Height of dam (m)	97.50
Length of dam (m)	447
Dam size	0.902 million m^3
Normal altitude (m)	147.50
Water surface elevation (m)	129
Mean depth (m)	28.5
Average annual volume (m^3)	1535×10^6
Average water residence time (days)	102
Average annual rainfall (mm)	1,197.60
Flood water level (m)	138
Water supply water level (m)	84
Emergency water supply capacity	496.00×10^6
Basin area (Km^2)	6,642.00
Total storage capacity (m^3)	$2{,}750 \times 10^6$
Active capacity (m^3)	$1{,}789 \times 10^6$
Effective storage (m^3)	$1{,}789 \times 10^6$
Active hydroelectric power generation (kW)	412×10^3
Design discharge volume (m^3/s)	16,200
Maximum discharge quantity (m^3/s)	20850

reservoir depth. The longitudinal clines were designated as three distinct zones: lacustrine *(Lz)*, transition *(Tz)*, and riverine *(Rz)*. This total waterbody catchment area of 6642 km^2 is further divided into distinct subwatersheds: 1) reservoir subwatershed (498 km^2), 2) Han River subwatershed (5484 km^2), 3) Jaecheon stream (461 km^2), 4) Gogyo streams (30 km^2), and 5) Dongdal and Gwang streams (169 km^2). The range of catchment area elevation is 115-1559 m with average hillslope of 36.9%. According to the land use pattern of the watershed area, 82.3% (5469 km^2) is forest area and only 12.2% (811 km^2) is under agricultural use [37]. The datasets used in this study were obtained during 1992-2016 from the National Institute of Environmental Research (NIER).

Physicochemical Water Quality Analysis

During this study, 18 physicochemical water quality factors were measured from three sampling stations during 1992-2016. The summary statistics and detail of parameters considered during the study are specified in Table 2. pH, dissolved oxygen, temperature, electrical conductivity, and Chl-a were recorded at the spot of monitoring stations by using the multi-parameter water quality sensors having probes dedicated for the factors (YSI Sonde 6600, Environmental monitoring system, Ohio, USA). Total coliform bacteria were measured as per the standard method opted for by APHA [38]. Total nitrogen (TN) and total dissolved nitrogen (TDN) were chemically evaluated by following the second derivative method followed by sample digestion in persulfate solution [39-40]. Ammonia nitrogen (NH_4-N) and nitrate nitrogen (NH_3-N) were assessed by phenate method and ion chromatography, respectively. The next step followed was the filtration of the extract from the source

Table 2. Mean and standard deviation of water quality parameters in three zones of Chungju Dam, 1992-2016.

Parameter Category	Water quality parameters	Abbreviations and units	Mean±standard deviation (Range)		
			Rz	Tz	Lz
Physico-chemical	pH	pH	8.09±0.41 7.1 - 9.5	8.00±0.44 4 - 9.2	7.99±0.44 6.3 - 9.5
	Dissolved oxygen	DO (ºC/L)	10.78± 2.41 4 - 17.5	10.24±2.29 4.1 - 15.5	9.14±2.67 3.1 - 22.9
	Water temperature	T (ºC)	14.44±7.8 1 - 27.2	14.14±6.95 2 - 27.2	13.53±6.80 2 - 29
	Biological oxygen demand	BOD (ºC/L)	1.35±0.37 0.5 - 2.8	1.26±0.32 0.3 - 2.5	0.89±0.37 0.3 - 2.6
	Chemical oxygen demand	COD (ºC/L)	2.18±0.43 1 - 3.6	2.10±0.43 1 - 3.7	2.19±0.51 1.1 - 3.7
Fecal Indicator Bacteria	Total number of E. Coli	TNEC	43.43±188.04 0 - 2200	18.21±42.72 0 – 500	317.29±1581.48 0 - 16917
Solids and visibility	Total suspended solids	TSS (ºC/L)	5.01±6.98 0.2 - 63.9	3.01±3.88 0.2 - 35.9	2.65±5.81 0.2 - 92.2
	Electrical conductivity	EC (µS/cm)	224.75±42.39 130 – 383	209.82±33.61 120 – 469	196.16±32.64 90 - 351
	Secchi disk depth *	SDD (m)	0.27±0.41 -1.05 - 1.46	0.46±0.37 -0.79 - 1.46	0.51±0.33 -1.20 - 1.46
Nutrient regime	Total nitrogen	TN (ºC/L)	2.38±0.57 1.13 - 4.92	2.29±0.53 0.86 - 4.92	2.35±0.69 1.43 - 6.98
	Total phosphorus	TP (µg/L)	22.85±14.08 1 – 117	19.49±10.63 1 – 84	21.78±21.89 0 - 273
	Total nitrogen total phosphorus ratio	TN:TP ratio	160.09±286.34 20.23 - 3892	182.55±304.19 35.55 - 4496	179.48±373.61 0 – 6148
	Total dissolved nitrogen	TDN (mg/L)	2.10±0.38 1.07 - 3.67	2.03±0.32 1.29 - 3.13	2.16±0.41 1.10 - 4.09
	Ammonia nitrogen	NH4-N (mg/L)	0.04±0.048 0 - 0.63	0.03±0.03 0 - 0.16	0.10±0.12 0 - 0.89
	Nitrate nitrogen	NO3-N (mg/L)	1.87±0.57 0.32 - 4.28	1.82±0.53 0.22 - 4.20	1.69±0.49 0.05 - 3.97
	Total dissolved phosphorus	TDP (µg/L)	16.37±11.40 0 – 94	13.68±8.23 0 – 44	11.18±7.88 0 – 47
	Phosphate phosphorus	PO4-P (µg/L)	21.02±161.58 0 – 2264	8.22±7.50 0 – 74	5.38±5.75 0 – 49
	Chlorophyll-a	CHL-a (µg/L)	4.57±4.38 0 - 25.2	3.28±3.22 0 - 31.1	3.44±4.27 0.2 - 28.2

* Secchi disk depth (SDD) was calculated by using the empirical equation of SDD = 0.76 – Log_{10} (TSS) [73]

sample of water through GF/C filters. The phosphorus and its allied chemical species – total phosphorus (TP), total dissolved phosphorus (TDP), and phosphate phosphorus (PO_4-P) – were analyzed by the ascorbic acid method that was followed by persulfate oxidation [40-41]. Total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) were analyzed according to standard methods described by [40]. Secchi disk depth (SDD) was calculated by using the empirical equation of total suspended solids (TSS), and the formula was expressed as $0.76 \times \log_{10}$ (TSS). According to standards proposed, the nutrient analyses were repeated three times for precision and the estimation of BOD, COD, and TSS was performed twice [38, 42].

Water Pollution Index (WPI)

Chemical health assessment was evaluated by use of a modified multi-metric model of water pollution index (WPI_{KR}). It was adapted from nutrient pollution index (NPI) approach of the same index modified after Dodds et al. [43] in the USA and Lee and An [44] in South Korea. Basically, it consists of 07 metrics/ parameters (Table 3). The WPI_{KR} metrics (M_{1-7}) used for chemical water health status are M_1: total nitrogen (mg/L); M_2: total phosphorus (µg/L); M_3: ambient ratios of TN:TP; M_4: biological oxygen demand (mg/L); M_5: total suspended solids (mg/L); M_6: electrical conductivity (µS/cm); and M_7: Chl-a (µg/L). It is based on some of the crucially important parameters that have proven effective on changing water quality for longer terms. The scoring criteria ascribed to every single metric was established for limits demarcated after following the third of observed distributions of obtained values. Consequently, the entrusted scoring criteria for every metric (M) was either 5, 3, or 1 score, respectively, depending upon the role of each water quality factor on the overall chemical health status of water. Based on the obtained scores, the concluding chemical health evaluation of each sampling station was calculated next to attain the total scores by summing up all the metric scores. Finally, it led to the decisive classification of each site as excellent (Ex. 31–35), good (G. 25–29), fair (F. 19–23), poor (P. 13–17), or very poor (VP. 07–11).

Trophic State Index Deviation (TSID)

The trophic state index deviation (TSID) was calculated by using the following formulae derived from Carlson [14], and the relations are shown by the following equations:

$$TSI\ (TP) = 14.42 Ln\ (TP) + 4.15 \quad (1)$$

$$TSI\ (TN) = 14.43\ Ln\ (TN) + 54.45 \quad (2)$$

$$TSI\ (SD) = -14.41\ Ln\ (SD) + 60 \quad (3)$$

$$TS\ I(Chl) = 9.81\ Ln\ (Chl) + 30.6 \quad (4)$$

Statistical Analysis

The obtained datasets were subjected to multivariate data analysis techniques such as principal component analysis (PCA), cluster analysis (CA), correlational analysis, and Mann-Kendall (MK) trend test. We also analyzed the datasets for spatio-seasonal and inter-annual variations of selected water quality parameters. Most of the data analyses were carried out using the Sigma Plot [45] version 10 (Systat. Software Inc; USA) and PAST [46]. Means and standard deviations were calculated using the PAST software as well as it also rendered to run the MK trend test, CA, and PCA.

Results and Discussion

Spatio-Seasonal Trend Analysis

Seasonal trends in water quality factors are primarily maneuvered by the precipitation patterns, and this was very evident in all the zones of Chungju Reservoir (Fig. 3, Table 2). The summer monsoon rainfall (July-August) mainly influences precipitation patterns in South Korea, wherein almost 70% of rainfall occurs and shows conspicuous hydrological changes in all types of water bodies. The study of rainfall pattern and water quality factors during 1992-2016 showed diverse changes in different factors, e.g., pH recorded the highest in proceeding months of September and October in all the zones. The DO and WT manifested the classical inverse relationship. Since most downpour occurs during July-August, therefore, monsoon precipitation was decisively influencing; otherwise, most of the physiochemical

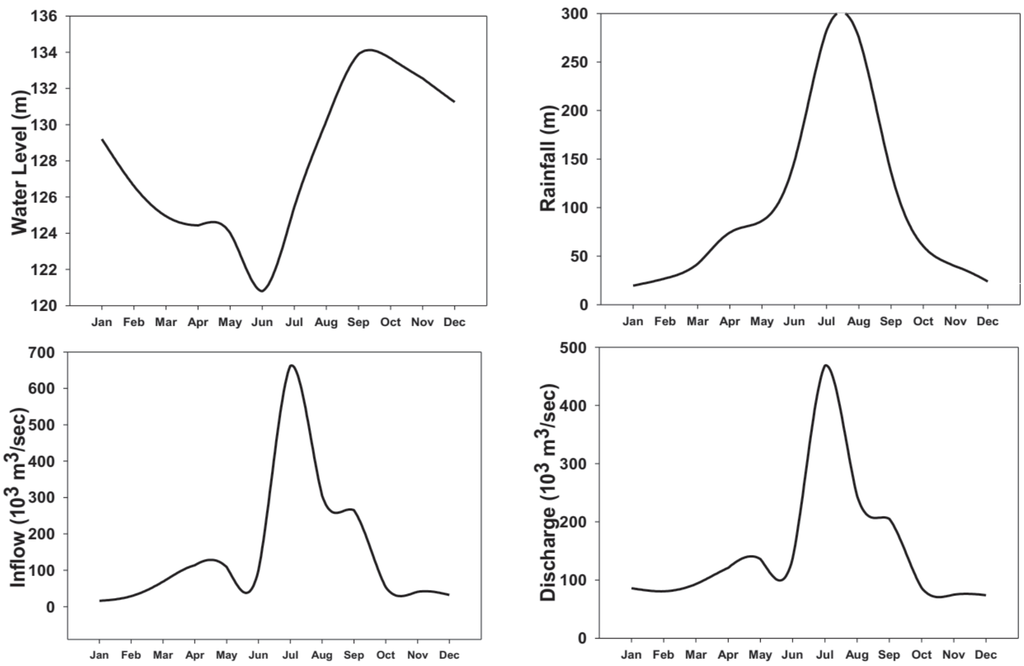

Fig. 2. Seasonal dynamics of water level, rainfall, inflow, and discharge in Chungju Reservoir, 1992-2016.

water quality factor activities were identical. The BOD showed almost no effect of rainfall, but in *Tz* and *Rz* it was higher as compared to the *Lz*. Conversely, the COD showed an unblemished increase after the monsoon period, which indicated the transport of more chemical-borne matter along with the runoff waters entering the lake environment. However, the overall COD level was well below alarming limits. TSS transport into the reservoir – especially higher in the *Rz* – implied higher siltation and it was mainly governed by the summer monsoon rainfall. The EC in *Lz* was almost similar but showed a decline in *Rz*, wherein the TSS was higher.

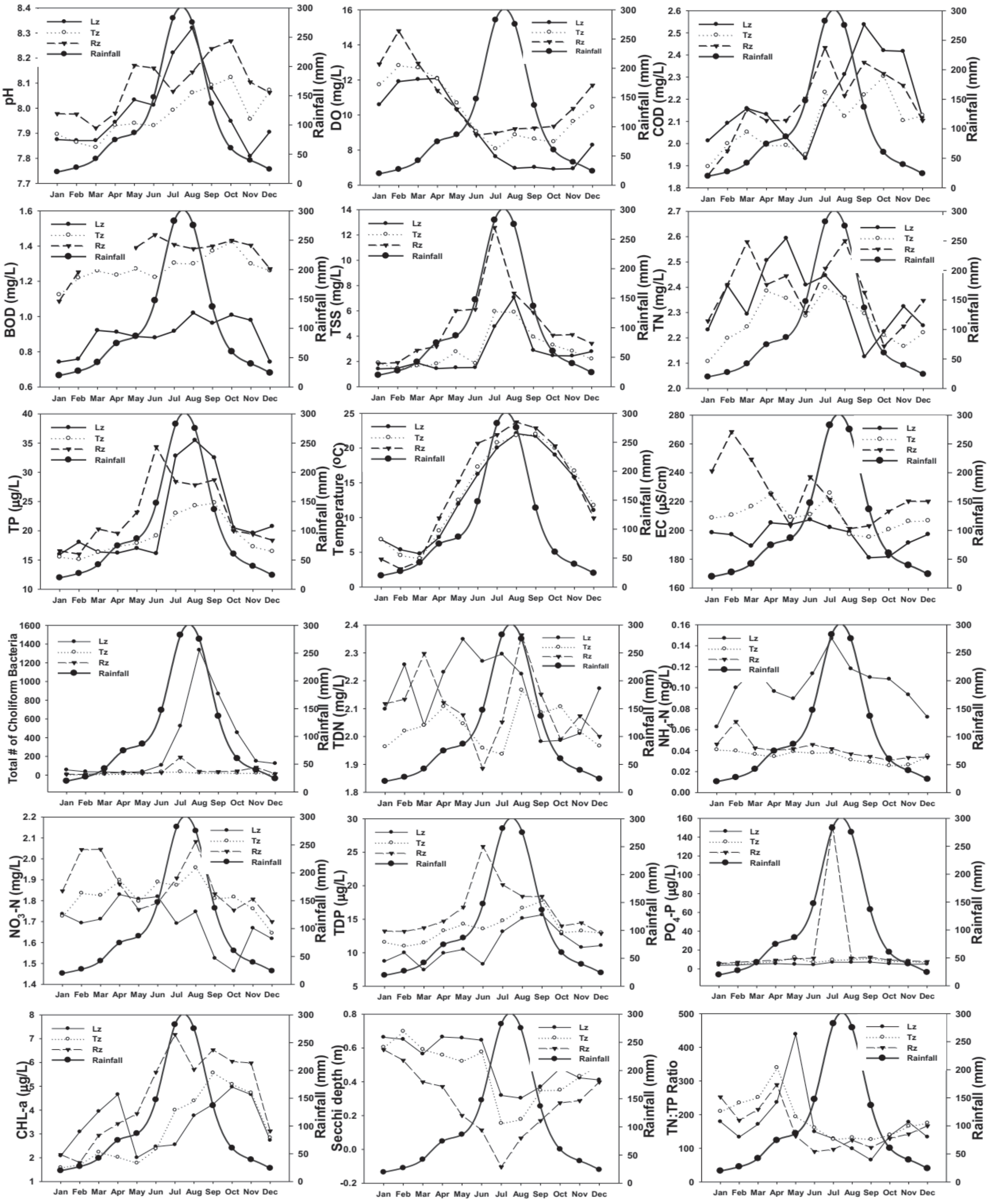

Fig. 3. Seasonal and spatial analysis of water quality parameters in *Lz, Tz*, and *Rz* of Chungju Reservoir, 1992-2016.

Table 3. Chemical health assessment of Chungju Dam based on modified multi-metric water pollution index (WPI) during 1992-2016.

Category	Model metrics (M)	Scoring criteria			Mean ± standard deviation scores		
		5	3	1	*Rz*	*Tz*	*Lz*
Nutrient Regime	M_1: Total Nitrogen (mg/L)	<1.5	1.5-3.0	>3	2.38±0.57 (3)	2.29±0.53 (3)	2.35±0.69 (3)
	M_2: Total Phosphorus (µg/L)	<30	30-100	>100	22.85±14.08 (5)	19.49±10.63 (5)	21.78±21.89 (5)
	M_3: TN:TP ratio	>50	20-50	<20	160.09±286.34 (5)	182.55±304.19 (5)	179.48±373.61 (5)
Organic Matter	M_4: Biological Oxygen Demand (mg/L)	<1	1-2.5	>2.5	1.35±0.37 (3)	1.26±0.32 (3)	0.89±0.37 (5)
Ionic Contents and Solids	M_5: Total Suspended Solid (mg/L)	<4	4-10	>10	5.01±6.98 (3)	3.01±3.88 (5)	2.65±5.81 (5)
	M_6: Electrical Conductivity (µS/cm)	<180	180-300	>300	224.75±42.39 (3)	209.82±33.61 (3)	196.16±32.64 (3)
Primary Production Indicator	M_7: Sestonic Chlorophyll (µg/L)	<3	3-10	>10	4.57±4.38 (3)	3.28±3.22 (3)	3.44±4.27 (3)
	Final Scores (Model Criteria of WPI)				25	27	27
	Water Quality Criteria				Good	Good	Good

TNCB showed a huge variation during monsoon rainfall, especially in the *Lz* and lesser or no changes in *Rz* and *Tz*. Coliform bacteria level is used as an important water quality indicator, which shows the contamination of human fecal matter [47]. The higher the TNCB, the greater the likelihood of fecal contagion, and henceforth greater threats of waterborne diseases [48]. The TN inputs in all the zones were similar until the monsoon period, and then showed a decline in the aftermath of increased rainfall. TP, however, was continuously shadowing the higher peak of monsoon rainfall that displayed that the main carrier of higher P loading into the reservoir was none other than the monsoon rainwater that carried most of the P from the catchment areas and was transported in the reservoir [49-50]. Seasonal concentrations of other nitrogen species such as TDN, NH_4-N, and NO_3-N were different from the comportment of N in the three zones, e.g., TDN showed promising increments with rainfall in the *Rz*, but in *Lz* it showed a peak in the preceding months of monsoon. On the other hand, NO_3-N was higher during most of the months, along with monsoon in the *Rz*. The values of PO_4-P and TDP were almost similar in all three zones, with a difference in the levels of TDP that were diluted because of the monsoon. In approximation with TP, the sestonic Chl-a levels were also mainly influenced by the monsoon rainfall pattern in all zones, with Rz being the most favorite place for the favorable growth of sestonic Chl-a. It showed a conspicuous decline in the proceeding period of monsoon. The SDD was the lowest during the monsoon rainfall period. The ambient ratios of TN:TP were inversely proportional to the rainfall pattern, but still sufficiently higher.

Spatial and seasonal analysis of Cungju Reservoir revealed heterogenic variations among the water quality factors in the zones showing longitudinal modifications from headwater (*Rz*) towards the dam site (*Lz*). Chl-a and TP were higher in the riverine zone as compared to other parts, which clearly indicates higher TP loads from the inflowing currents. The longitudinal difference in the levels of nutrient contributing factors (TP, TN), resultant algal biomass in terms in Chl-a, and increased reception of solid contents as TSS has been reported in other studies [51-53]. Distinct and huge longitudinal gradient among three zones (*Lz* – *Tz* – *Rz*) was not, however, noticed in the case of Chungju Reservoir.

Annual Trends in Water Chemistry

The annual variations showed distinct heterogeneities in nutrient contributing factor distribution, solid content loads, COD, and Chl-a concentrations in the ambient lake environment (Fig. 4). The annual concentrations of sestonic Chl-a, TN, TP, and COD were primarily affected by the annual precipitation level in the catchment area. Based on annual precipitation rates during the study, interchangeabe flood and drought conditions prevailed, with 1998, 2003, and 2011 being the high flooding years. The rainfall pattern is such a huge influencing factor that it was strikingly played down with the annual water quality parameter trends such as during drought years, when water pH dropped below neutral (6.4) and vice versa (9.6). Therefore, it could be inferred that selected water quality factors changed in a synchronous manner with the flood and drought years. BOD annual variations showed asynchronous behavior with the flood, drought, and average rainfall years. On the other hand, COD showed approximating increases in levels with increasing amounts of rainfall. COD showed a gradual increase

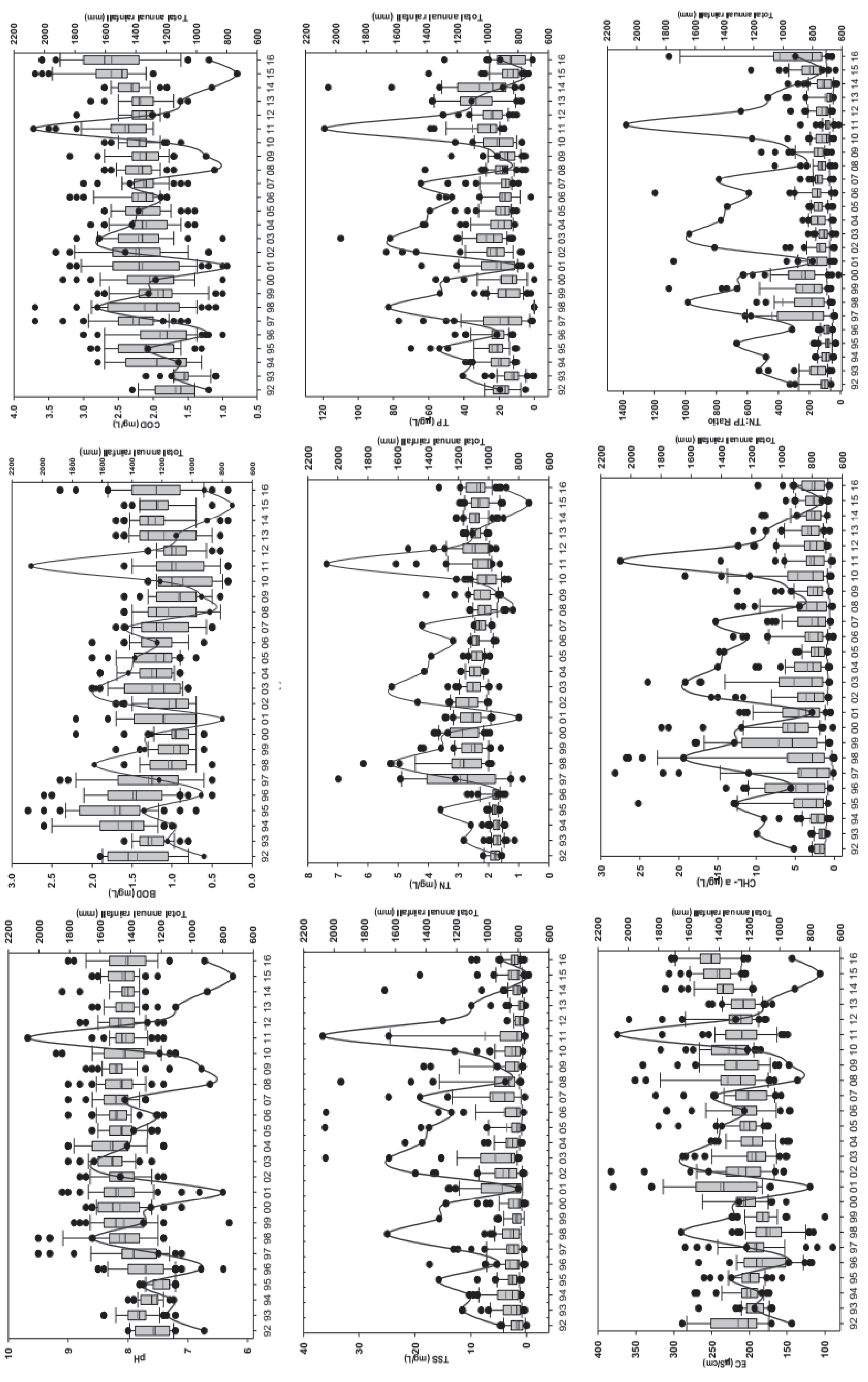

Fig. 4. Inter-annual trends of selected water chemistry parameters in relation to annual rainfall, 1992-2016.

Table 4. Pearson correlation analysis between water quality parameters in Chungju Reservoir, 1992-2016

Parameters	pH	DO	BOD	COD	TSS	TN	TP	TN:TP	T	EC	TNCB	TDN	NH_4-N	NO_3-N	TDP	PO_4-P	CHL-a	CHL:TP	CHL:TN	TDN:TDP	BOD:COD	SD
pH	1.00																					
DO	0.06	1.00																				
BOD	-0.11	-0.04	1.00																			
COD	0.16	-0.11	**0.19**	1.00																		
TSS	0.06	-0.11	**0.18**	**0.20**	1.00																	
TN	**0.20**	0.10	**-0.20**	0.15	0.09	1.00																
TP	0.06	**-0.17**	0.05	**0.23**	**0.18**	0.10	1.00															
TN:TP	-0.002	0.08	-0.11	-0.06	-0.06	**0.31**	-0.26	1.00														
T	**0.25**	**-0.65**	0.14	**0.19**	**0.22**	0.02	0.25	-0.11	1.00													
EC	0.10	0.20	0.04	0.09	-0.08	-0.02	-0.05	-0.03	-0.16	1.00												
TNCB	0.04	-0.14	-0.02	0.04	-0.003	-0.02	-0.002	-0.01	0.07	0.05	1.00											
TDN	0.001	0.06	0.03	0.08	0.12	**0.86**	0.06	**0.22**	-0.02	-0.06	-0.01	1.00										
NH_4-N	-0.02	**-0.17**	**-0.19**	0.0005	-0.004	0.02	0.04	-0.01	0.003	-0.03	0.08	0.17	1.00									
NO_3-N	0.11	0.11	-0.05	0.0004	0.10	**0.55**	-0.02	0.01	-0.005	-0.002	-0.05	**0.75**	-0.06	1.00								
TDP	0.04	-0.09	**0.24**	0.11	0.14	0.13	0.74	**-0.40**	**0.24**	-0.05	-0.04	0.007	-0.08	-0.07	1.00							
PO_4-P	-0.03	-0.01	0.07	0.004	0.005	0.04	0.10	-0.05	0.08	0.03	-0.007	0.02	-0.01	-0.04	0.16	1.00						
CHL-a	**0.19**	-0.14	0.17	**0.21**	0.12	0.15	0.14	-0.03	**0.29**	-0.08	-0.06	0.03	-0.06	0.03	0.26	0.10	1.00					
CHL:TP	0.10	-0.03	0.03	0.08	-0.006	**0.17**	-0.19	**0.51**	0.05	-0.09	-0.04	0.04	-0.002	0.03	-0.24	-0.007	**0.55**	1.00				
CHL:TN	0.15	-0.16	**0.23**	**0.18**	0.10	-0.08	0.12	-0.08	**0.30**	-0.06	-0.07	-0.12	-0.06	-0.11	0.22	0.09	0.93	0.47	1.00			
TDN:TDP	-0.06	0.04	-0.11	-0.03	-0.08	0.04	-0.28	**0.38**	-0.11	0.11	-0.02	0.11	0.006	0.11	-0.44	-0.04	-0.09	0.29	-0.09	1.00		
BOD:COD	**-0.23**	0.02	**0.78**	**0.41**	0.05	**-0.30**	-0.07	-0.07	0.01	-0.04	-0.04	0.005	**-0.19**	-0.05	0.17	0.06	0.01	-0.03	0.09	-0.08	1.00	
SD (m)	-0.09	0.18	**-0.27**	**-0.24**	**-0.72**	-0.11	-0.21	0.06	**0.33**	0.06	-0.02	-0.07	0.09	-0.16	-0.14	-0.02	-0.22	-0.02	**-0.19**	0.08	-0.11	1.00

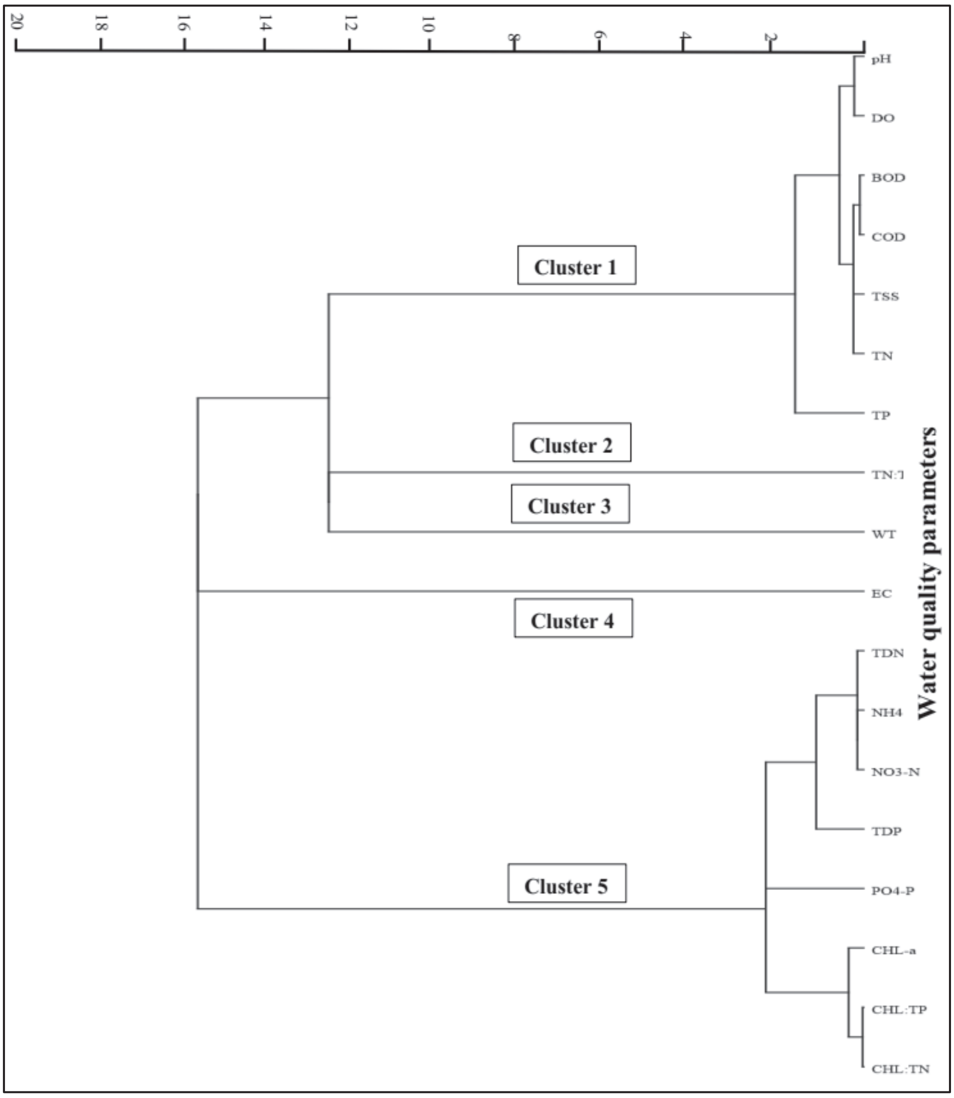

Fig. 5. Dendrogram showing the hierarchical cluster analysis of selected water quality parameters of Chungju Reservoir, 1992-2016.

during the study period 1992-2016. The TSS loads provided insight into the collective and individual maximum rainfall events that are evident of higher TSS loads occasionally. TN and allied nitrogen species manifested annual patterns in relation to the rainfall, e.g., during dry years of 1992-96 it showed no distinct changes, but with increasing rainfall the TN loads also increased and annual means concentration of TN remained >2.0 mg/L. The rainfall significantly influences TP, and Chl-a showed a similar annual trend. It also showed that seasonal and annual increases in TP loads are mainly contributed to the agricultural activities that are being transported into the reservoir due to rainfall events. Annual values of ambient TN:TP ratios were decreased during the flood years, which shows that the reservoir was diluted by higher rainfall events. This type of inter-annual variation of pH, nutrients, and sestonic Chl-a disclosed how rainfall patterns maneuver water quality and transport the effects of intensive agricultural and industrial activities in the watershed areas [2, 53-56].

Reservoir Inflow and Discharge Patterns

The seasonal and long-term patterns of flow regime were mainly defined by the Asian monsoon patterns in the catchment area (Fig. 2). Summer monsoon season (July-August) is the period of highest rainfall events, wherein 44.5 mm occurred during July and 35.2 mm during August. This monsoon rainfall amount was 37% of the total annual rainfall (inclusive of drought and flood years), which evidently proves massive precipitation during these two months. On the contrary, the lowest rainfall was observed during the winter season (December-January), with 4.53 and 4.52 mm, respectively. In exoreic reservoirs, rainfall volume determines the inflow and discharge dynamics. During 1992-2016, the mean water level reached its lowest (120.79 m) before the beginning of monsoon rainfall in order to store maximum inflowing water to mitigate floods and, as a result, the postmonsoon mean water level in September reached 133.88 m.

Table 5. Mann-Kendall trend test on Chungju Reservoir water parameters showing trends, 1992-2016.

Parameter category	Water quality parameters	S value	Z value	P value	Trend
Physico-chemical	pH	67848	7.92	2.31	Significantly increasing
	DO	37007	4.31	1.65	Significantly increasing
	T	7262	0.84	0.39	No trend
	Total # of Coliform Bacteria	-92353	10.77	4.85	Significantly decreasing
	BOD	-51941	6.11	1.06	Significantly decreasing
	COD	95558	11.16	6.75	Significantly increasing
Solids and visibility	TSS	-21818	2.54	0.01	Significantly decreasing
	EC	104439	12.16	5.19	Significantly increasing
	SD (m)	21818	2.54	0.01	Significantly increasing
Nutrient regime	TN	51054	5.94	2.8	Significantly increasing
	TP	27316	3.18	0.0014	Significantly increasing
	TN:TP	-3847	0.45	0.65	No trend
	TDN	-7531	1.93	0.053	No trend
	NH4-N	16997	2.39	0.017	Significantly increasing
	NO3-N	-34544	4.85	1.21	Significantly decreasing
	TDP	546	0.139	0.89	No trend
	PO4-P	-5949	1.24	0.22	No trend
	CHL-a	3508	0.41	0.68	No trend
Ratios	CHL:TP	-10960	1.28	0.20	No trend
	CHL:TN	-17339	2.16	0.031	Significantly decreasing
	TDN:TDP	-5096	1.3	0.19	No trend
	BOD:COD	-116915	13.68	1.27	Significantly decreasing

In approximation with seasonal rainfall events, the lowest inflow was observed during January and February, i.e., 16.02×10^3 m^3/sec and 28.86×10^3 m^3/sec, respectively, whereas the highest inflow occurred during monsoon season (July-August), i.e., 661.99×10^3 m^3/sec and 305.44×10^3 m^3/sec, respectively. The discharge dynamics were also mainly determined by the seasonal rainfall patterns and were lowest in November and December, i.e., 74.96×10^3 m^3/sec and 73.89×10^3 m^3/sec, respectively, whereas the highest was recorded during July and August as 468.34×10^3 m^3/sec and 244.42×10^3 m^3/sec, respectively. This observation indicated that the inflow and discharge dynamics of exoreic reservoirs are directly regulated by the seasonal rainfall events. It also indicates the success of Chungju Reservoir in mitigating the impending flood events in the locality.

Health Assessment by Water Pollution Index (WPI)

Modified multi-metric water pollution index (WPI_{KR}) was used for diagnosing chemical health status (Table 3). Comprised of 07 metrics (M_1-M_7), it included the most influential water quality factors which, if shifted in a disparaging way, could act as pollutants. The four most important groups are namely nutrient regime (TN, TP, and TN:TP), organic matter (BOD or COD), solid and ionic levels (TSS and EC), and primary productivity indication (Chl-a). The chemical concentration criteria of TN was set as oligotrophic (3.0 mg/L), mesotrophic (1.5–3.0 mg/L), and eutrophic (>3.0 mg/L). All three zones fell under the category of mesotrophic, with *Rz* showing the higher TN influx. In the same fashion, the TP criteria were oligotrophic (<30 µg/L), mesotrophic (30–100 µg/L), and eutrophic (>100 µg/L. All zones (*Rz*, *Tz*, and *Lz*) were under the oligotrophic category. Ambient water TN:TP ratios also displayed oligotrophic conditions at all the stations. The mean concentrations of sestonic Chl-a also approximated with the concentrations of TN, TP, and TN:TP ratios by confirming that *Rz*, *Tz*, and *Lz* were in the oligotrophic state. The mean BOD level was maximum in *Rz* (1.35 mg/L) and minimum at *Lz* (0.89 mg/L). The solid content loads showed that means TSS was the highest in

Rz (5.01 mg/L) and lowest in *Lz* (2.65 mg/L), whereas EC was observed <180 µS/cm at all the longitudinal. The obtained scores after the sum of all metrics led us to categorize the chemical health status of all the zones of the reservoir as good (*Rz*: 25, good; *Tz*: 27, good; *Lz*: 27, good) (Table 3). It also endorses that the sedimentation process in Rz may decrease the storage capacity as well as the gravitational flow of inflowing water as well as a great sink of nutrients. In the case of lakes and reservoirs, major nutrients (i.e., TN, TP, and ambient water TN:TP ratios) are identified as the vital elements liable for controlling water health and eutrophication status [46]. Previous researchers showed that higher ambient water TN:TP ratios are an indirect indicator of some nutrient limitations for Chl-a productions [51-58], and if TN:TP ratios are lower, they indicate increased nutrient pollutants leading to eutrophic conditions [43]. This sort of quality deterioration in chemical health is sumptuously supported by earlier researchers [53-54, 56-58, 59-61].

Pearson Correlation Analysis

The Pearson correlation indicated the absence of a strongly positive or significant correlation (above 0.7) among the majority of water quality parameters of Chungju Reservoir (Table 4). However, it has been shown that moderate and weak significant correlation exists among the various water quality factors. TN showed a weak positive correlation ($r = 0.31$, $P>0.01$), with TN:TP ratio and week negative correlation among TP and TN:TP ratios ($r = -0.26$, $P >0.01$). Chl-a showed weak positive correlation with TN and TP ($r = 0.15$, $r = 0.14$, $P>0.01$), respectively. Also, Chl-a was weakly positively correlated with TDP ($r = 0.26$, $P>0.01$) as compared to PO_4-P, TP, or TN, and allied chemical species. Among the ambient water ratios of TDN:TDP and TN:TP, weak positive correlation ($r = 0.38$, $P>0.01$) was observed, which could be used to infer that the ambient ratios did not play a significant role in Chl-a productivity. TP showed a strong positive correlation with TDP ($r = 0.74$, $P>0.01$), whereas TN showed a strong positive correlation with TDN ($r = 0.86$, $P>0.01$), pointing toward the derivation of TP and TN by these allied chemical species. As anticipated, the negative correlation of DO with numerous other water quality parameters revealed the organic pollution persistence in Chungju reservoir that can be reflected as one of the main roots of chemical, ecological, and environmental degradation.

Trend Analysis Using the Mann-Kendall (MK) Trend Test

The Mann-Kendall (MK) statistical test is a non-parametric trend analysis method that has been widely used for trend detection in hydrological time series datasets. It is an effective tool for water resource planning and management, since it can extract useful information on the possibility of change in the tendency of water quality variables in the future. The significance of trends in water quality parameters of Chungju gave powerful insight to the existing and future trends in key regulatory factors such as TN, TP, Chl-a, BOD, COD, EC, TSS, and ambient ratios of nutrient contributing factors with Chl-a (Table 5). In the present study, pH, DO, COD, TN, TP, EC, NH_4-N, and SDD are significantly increasing in the ambient water. On the other hand, BOD, TSS, TNCB, NO_3-N, CHL:TN ratios, and BOD:COD ratios are observed to be significantly decreasing. WT, ambient water TN:TP ratios, TDN, TDP, PO_4-P, Chl-a, and CHL:TP ratios showed no significant trend. Thus it was inferred that nutrient contributing factors such as TN and TP were significantly increasing, whereas Chl-a showed no significant trend, implying that TN or TP are present in a state that is not supporting future eutrophication events. It is also supported by the decreasing trend in TSS and SDD. However, COD is observed to be increasing along with pH, which indicates increasing inflow of industrial and agricultural runoff. This test, therefore, stresses the efficient management of the catchment areas for better management of Chungju reservoir. It must be noted that trend analysis shown by the MK trend test does not necessarily imply the trend to be sustainable in the future as it mainly depends on the magnitude of variables used as well as the catchment system, which may face certain modifications due to anthropogenic activities [62-64].

Hierarchical Cluster Analysis (HCA)

We used HCA to show the sampled water quality factors with similar characteristics in Chungju to check the main sources attributed toward the parameters. Hierarchical agglomerative clustering technique is one of the most commonly used approaches to understanding the instinctive similarity relations between anyone variable with the entire dataset, and displays the results in the form of a tree diagram (a dendrogram) that depicts the proximity of variables to one another by reducing the dimensionality [65]. For clustering of water quality parameters, hierarchical agglomerated CA was carried out by using Ward's technique with squared Euclidean distance similarity measures [66]. The HCA yielded the water quality factors into five distinct clusters, with EC, WT, and TN:TP ratios acting as singular factors comprising distinct clusters (Fig. 5). In cluster 1, pH and DO showed similarity to one sub-cluster, indicating generic or mixed origin from the watershed. Similarly, in cluster 1, BOD, COD, TSS, and TN showed similarity rendering the observation that they were mainly contributed to by the industrial activities pointing toward the increased anthropogenic activities in the catchment areas. It also indicated the runoff waters transporting the pollutants into the reservoir. However, TP is part of cluster 1, performed differently and indicating that it mainly originated from the agricultural activities due to its allied chemical species along with contributions from industrial activities. In the case of clusters 2, 3, and 4, the TN:TP ratios, WT, and EC were observed to cluster singularly, showing that these factors were not affected by one source but can be attributed to generic origins, which may be either anthropogenic, industrial, or agricultural in nature. In cluster 5, TDN, NH_4-N, and NO_3-N appeared to be clustered as in sub-cluster 1, whereas CHL-a, CHL:TP ratios, and CHL:TN ratios were yielded to sub-cluster 2. However, PO_4-P was observed to act independently next to TDP, which again indicates the origin of phosphorus and allied species mainly from the agricultural sources, although not limited to a single source. Moreover, it was confirmed that for Chl-a production, TP is the limiting factor that gives insight into a gradual increase with the advancing years.

Principal Component Analysis (PCA)

Considering the complexity of the relationship between several water quality factors, it was inevitable to extract the confidential information and understanding of data structures of complex datasets without the use of principal component analysis (PCA). The principal components (PC) helped to classify the water quality factor loadings as strong, moderate, or weak in correspondence to their absolute loading strengths of >0.75, 0.75-0.50, and 0.50-0.30, respectively [67-68]. The detailed two-dimensional analysis of water quality parameters (Fig. 6) and correlation matrix of chemical components showed a diverse variance (Table 6). The first 07 components of PCA analysis showed 70.45% of the total variance in the Chungju water quality datasets. The first PC was mainly comprised of Chl-a and solids, which showed 15.89% variance. It also indicated that chances of eutrophication are far less during the premonsoon months, and that higher suspended solids loadings would give rise to siltation problem in the future due to increasing SDD visibility that is directly related with higher solids settlement in the lake. It also showed that the solids and chemicals being transported to the reservoirs were mainly carried along with the non-point sources such as runoff, and that a negative relationship between the DO and temperature showed the seasonal changes in the study area. The second PC showed that BOD and related chemical pollutants are decreasing, which indicates lower organic pollution, and it also showed an equilibrium among the nutrient component factors in terms of TN:TP ratios. It also showed that biological pollutants are mainly being contributed by anthropogenic activities. The third components mainly explained the nutrient contributing factors and showed that TP is acting as limiting factor. However, lower variance rules out the chances of eutrophication events in future due to the nutrients. These nutrient-contributing factors are mainly due to agricultural activities such as fertilizers and livestock production [60, 69]. It successfully explains the existing balance between the nutrient contributing factors as well as the Chl-a production during the whole year. The fourth component explains the industrial pollutants, which are in the mild strength, but it also implies that with the continuous addition of industrial effluents, it will keep on increasing the chemical loads, which is also indicative of increasing COD and pH in the ambient lake environment. In the seventh PC, moderate positive loading of TNCB indicates untreated or uncontrolled

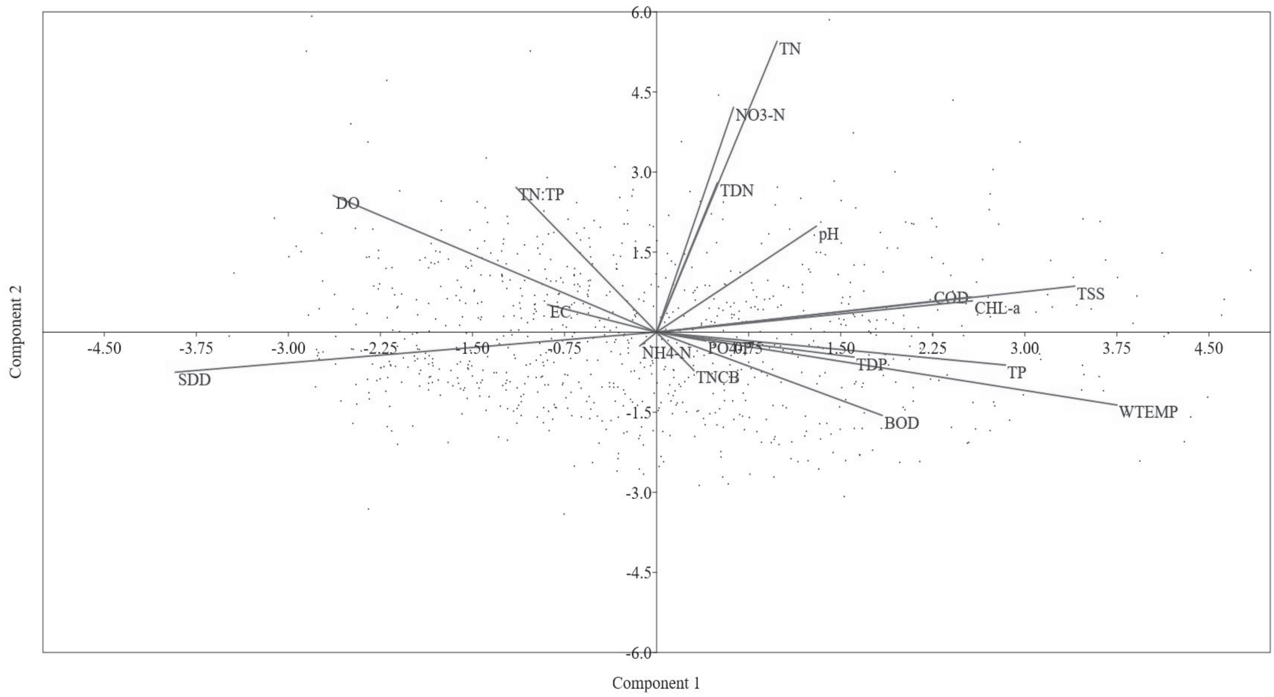

Fig. 6. Principal component analysis of Chungju Reservoir, 1992-2016.

Table 6. Principal components, their loading values, eigenvalues, and percent variance.

Variables	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
pH	0.25	0.38	-0.13	-0.08	0.28	-0.20	0.23
DO (mg/L)	**-0.44**	0.15	0.20	**0.43**	**0.57**	-0.03	-0.17
BOD (mg/L)	0.39	**-0.58**	0.30	**0.41**	0.06	-0.11	0.24
COD (mg/L)	0.43	0.24	-0.28	-0.07	0.26	-0.38	-0.05
TSS (mg/L)	**0.51**	-0.08	-0.31	**0.43**	-0.16	-0.29	-0.39
TN (mg/L)	0.12	0.69	-0.22	**0.40**	-0.03	0.26	0.19
TP (µg/L)	0.42	-0.14	**-0.50**	-0.09	0.29	0.39	-0.01
TN:TP ratio	-0.12	**0.50**	0.38	0.18	-0.36	-0.08	-0.07
Water Temp (ºC)	**0.65**	-0.07	-0.22	-0.26	-0.34	0.02	0.24
Conductivity (µS/cm)	-0.17	0.02	-0.01	0.08	**0.50**	**-0.46**	0.34
Total No. of *E. Coli Bacteria*	0.00	-0.02	-0.16	-0.17	-0.23	-0.35	**0.54**
TDN (mg/L)	0.05	0.30	-0.16	0.46	-0.12	0.26	0.26
NH_4-N (mg/L)	-0.06	0.12	-0.18	-0.27	-0.23	0.05	0.02
NO_3-N (mg/L)	0.04	0.38	-0.19	**0.56**	-0.06	0.24	0.30
TDP (µg/L)	0.35	-0.20	-0.25	0.01	0.30	**0.46**	0.02
PO_4-P (µg/L)	0.10	-0.05	-0.01	-0.01	0.10	0.15	0.09
Chlorophyll-a (µg/L)	**0.75**	0.24	**0.44**	-0.15	0.22	0.13	0.02
CHL:TP ratio	0.34	0.48	**0.64**	-0.04	-0.15	-0.02	-0.05
CHL:TN ratio	**0.72**	0.07	**0.48**	-0.24	0.24	0.06	-0.02
TDN:TDP ratio	-0.18	0.19	0.17	0.06	-0.18	-0.27	0.05
BOD:COD ratio	0.10	**-0.69**	**0.43**	0.42	-0.12	0.14	0.25
SDD (m)	**-0.63**	0.10	0.26	-0.42	0.16	0.30	0.25
Eigenvalue	**3.21**	**2.34**	**2.06**	**1.75**	**1.44**	**1.24**	**1.06**
% Variance	**15.89**	**11.59**	**10.20**	**8.64**	**7.11**	**6.11**	**5.22**
Cumulative % Variance	**15.89**	**27.47**	**43.36**	**52.00**	**59.11**	**65.22**	**70.45**

release of domestic and livestock effluents mixed with the ambient water, which can be ascribed to the municipal sewage as well as WWTPs. The fifth, sixth, and seventh PCs explained the data sets as 7.11%, 6.11%, and 5.22%, respectively, which showed that chemical and nutrient pollution events would not be severed if they occur but only if the existing set of conditions prevails [70-71].

Trophic State Index Deviation (TSID)

The seasonal and spatial TSID assessment displayed that there was huge zooplankton grazing during a whole year at all the sampling stations of Chungju Reservoir (Fig. 7). However, in premonsoon and monsoon periods, the infinitesimal presence of larger particles along with blue-green algae production was observed. However, *Lz* and *Rz* were shown to harbor the larger particles and blue-green algae, whereas the *Tz* was the main site for zooplankton grazing. TSID is a multidimensional phenomenon, which largely puts forth that no single nutrient factor can sufficiently be credited to measure the trophic state [14]. According to grazing theory, algal biomass will decrease and transparency will increase, which will lead to greater light penetration. This is also suggested that P is not the decisive factor in this condition. Even if the grazers regenerate the P, TSID will remain unchanged and is evidently supported in the present study in case of the spatial and seasonal trophic status of Chungju Reservoir. There is evidence that the transition from turbid state to grazing state was largely influenced by *Daphnia,* which resulted in the deviation from the upper right component to lower right component [11]. However, in some cases, even if TP is pronouncedly reduced, the Chl-a is lowered [72-74]. This is also attributed to zooplankton grazing, which again confirms that not a single nutrient can be responsible for the eutrophication of Chl-a production [75-78]. However,

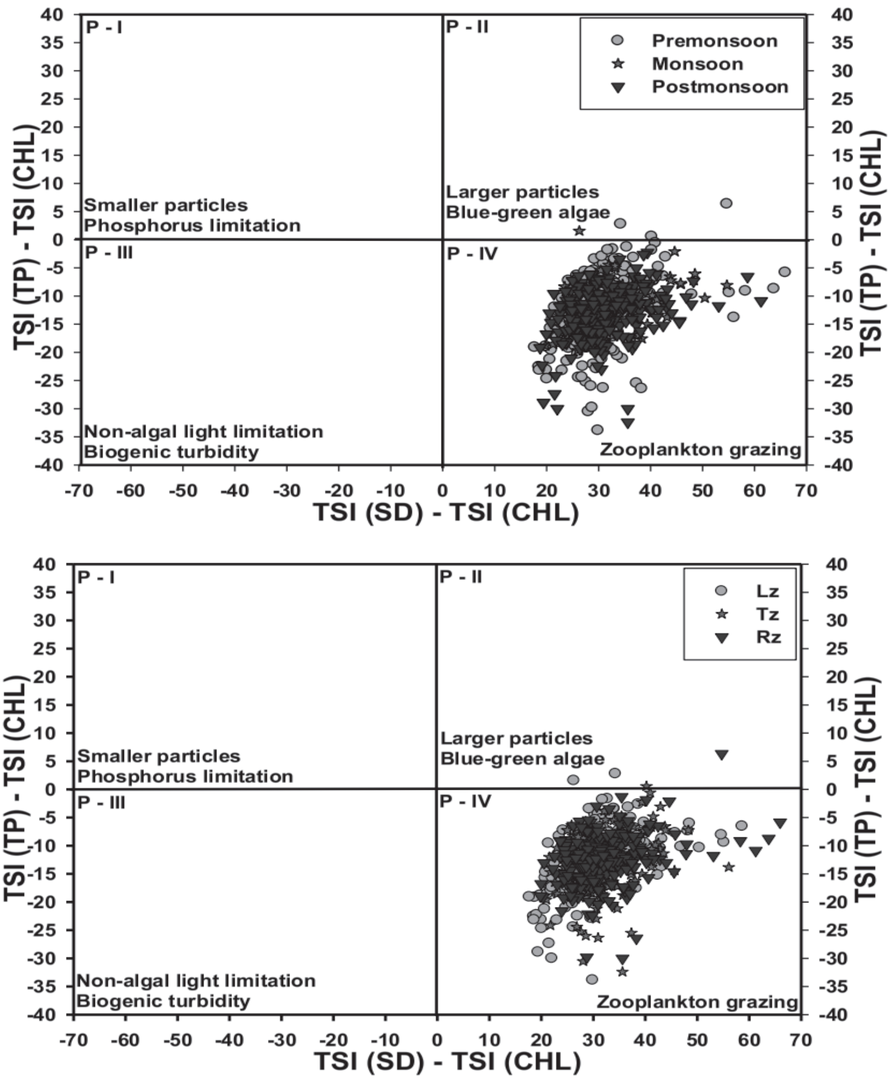

Fig. 7. Trophic state index deviation (TSID) during premonsoon, monsoon, postmonsoon (a), and *Lz*, *Tz*, and *Rz* (b) in Chungju Reservoir, 1992-2016.

in order to reveal an under-the-carpet situation, bioassays are required to be conducted to estimate the precise condition. These study results are different from the previous results, wherein it was shown as algal turbidity [74]. Algae production may be ascribed to non-algal light attenuation, which was mainly influenced by the suspended solids. The increase in SDD is also an indication of zooplankton grazing in all the zones of the reservoir. However, most of the Korean reservoirs have shown non-algal turbidity [2], which might have been the case in the beginning, but later on the trophic status shifted toward the lower component, i.e., zooplankton grazing.

Conclusion

This study was performed to estimate water quality status of the largest freshwater reservoir in South Korea by using some multivariate analytical techniques. Our study confirmed that the overall water quality of Chungju Reservoir was in a good state, and it was confirmed by the application of WPI and shown that chemical pollutants mixed with agricultural runoff as well as domestic sewage originating from the municipality and WWTPs are gradually degrading overall quality. Based on seasonal and annual analyses, a strongly influential factor on water quality alteration was the monsoon rainfall, which is also the main culprit for the transport of chemicals and nutrient contributing factors into the reservoir from a plethora of sources such as domestic sewage, WWTPs, industrial effluents, livestock, and crop production activities. Furthermore, the reservoir was receiving an increased amount of suspended solids and these solids are settling, which may cause a siltation problem leading to decreased water storage capacity of the country's largest water reservoir. The Mann-Kendall test showed that pH, COD, TN, TP, NH_4-N, and NO_3-N were gradually increasing in the reservoir, implying an impending nutrient-rich environment detrimental to the biological component of the reservoir. But the chances of eutrophication were diminutive, although with occasional blooms in the postmonsoon season due to the huge transport of nutrients. The PCA and CA provided useful insight to the complex datasets by showing that overall water quality deterioration could be ascribed to the non-point source pollutants originating mainly from the domestic and agricultural runoff from the catchment area. Moreover, the results given by CA were confirmed by PCA results. Such a big amount of pollutants is originating from such diffuse sources as domestic and agricultural runoff and hence is uncontrollable in many countries [79-80]. This study persuasively contributes in assessing and predicting the water quality dynamics – especially chemical and nutrient inputs, giving valuable insight into the chemical health status of the reservoir. Since the reservoir is very crucial for domestic water supply, integrated monitoring and control strategies for anthropogenic activities, which are never limited to agriculture and industry, is required to continuously monitor environmental degradation, and people should be encouraged to play their role in maintaining the water quality status for a sustainable water supply.

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Conflict of Interest

The authors declare no conflict of interest.

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