



Comparative Study of Physicochemical Parameters of Surface Water and Groundwater Samples

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Peer Review Information	Abstract
<i>Submission: 12 Jan 2015</i> <i>Revision: 27 Feb 2015</i> <i>Acceptance: 14 March 2015</i> Keywords <i>surface water; groundwater; physicochemical parameters; water quality index; hydrochemistry</i>	This methodology paper presents a comparative framework for evaluating physicochemical differences between surface water and groundwater. A balanced design of ten surface-water locations and ten groundwater locations, sampled during pre-monsoon and post-monsoon periods, is proposed. Field measurements include temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO), while laboratory analyses include turbidity, alkalinity, total hardness, calcium, magnesium, chloride, sulphate, nitrate and fluoride. Descriptive statistics, source-wise comparison, correlation analysis and a weighted water quality index (WQI) are used to interpret overall quality. Literature available up to 2015 shows that surface water is commonly more responsive to runoff and direct anthropogenic loading, whereas groundwater chemistry is strongly influenced by mineral-water interaction, residence time and local contamination pathways. The proposed procedure integrates standardized sampling, laboratory quality control and statistical interpretation to produce a reproducible comparison suitable for academic and environmental monitoring studies. Since no primary laboratory dataset was supplied, the numerical values in the Results section are explicitly presented as an illustrative methodology-validation dataset rather than measured field results

Introduction

Water quality depends on the source, catchment characteristics, geology, residence time, hydrological connectivity and human activity. Surface waters such as rivers, lakes and reservoirs are directly exposed to runoff, suspended matter, wastewater discharge and seasonal changes, while groundwater is buffered by soil and aquifer materials but can accumulate dissolved ions through prolonged rock-water interaction. A direct source-wise comparison is therefore useful for distinguishing short-term surface contamination from mineralization or persistent subsurface contamination.

Bhardwaj and Singh (2011) demonstrated the value of analyzing surface water and

groundwater together, showing that differences in EC, TDS, hardness, bicarbonate and major ions can reveal both natural and anthropogenic controls. River studies in India have also shown that physicochemical parameters respond to industrial and urban inputs (Chandra et al., 2011). Groundwater investigations have similarly emphasized the roles of hardness, major ions, nitrate and TDS in determining drinking-water suitability (Rajankar et al., 2011; Dudeja et al., 2011).

The objective of the present methodology is to provide a reproducible protocol for (i) collecting paired surface-water and groundwater samples, (ii) measuring common physicochemical variables, (iii) comparing source-dependent

patterns statistically, and (iv) integrating multiple parameters using WQI. The framework is suitable for small regional studies where both sources are used for domestic, agricultural or municipal purposes.

Literature Review

Earlier investigations consistently show that groundwater and surface water should not be interpreted using the same assumptions. Patil and Patil (2011) reported strong variation in EC, TDS, alkalinity and hardness among open-well and tube-well groundwater samples, while Balan et al. (2012) used WQI to summarize groundwater suitability in Chennai. Sajil Kumar and James (2013) linked groundwater chemistry to physicochemical sources, and Elangovan and Dharmendirakumar (2013) documented seasonal groundwater quality changes along an urban river corridor.

Surface-water studies emphasize direct exposure to runoff and urban inputs. Ravikumar et al. (2013) used a multi-parameter WQI for Bangalore lakes and showed that TDS, EC,

alkalinity, hardness and chloride strongly affected the index. Pandey and Kumar (2015) demonstrated pronounced spatio-temporal variation in urban surface-water resources. Such findings support seasonal sampling and the measurement of both mineralization indicators and oxygen/turbidity-related parameters.

Hydrogeochemical work also shows that surface-water-groundwater interaction can modify source signatures. Brindha et al. (2014) identified interaction between river water and groundwater using major-ion chemistry, while Singh et al. (2014) used hydrochemical characterization to explain groundwater quality in the Indo-Gangetic plain. Krishna Kumar et al. (2015) and Batabyal and Chakraborty (2015) further demonstrated the usefulness of WQI for integrating complex groundwater datasets. Collectively, these studies justify a design combining conventional physicochemical analysis, seasonal replication, WQI and statistical comparison.

Table 1. Summary of Previous Studies on Surface Water and Groundwater Quality Assessment

Study	Water source / focus	Key methodological relevance
Bhardwaj & Singh (2011)	Surface + groundwater	Direct source comparison; major ions and trace elements
Ravikumar et al. (2013)	Surface water	Multi-parameter WQI and seasonal monitoring
Brindha et al. (2014)	Surface-groundwater interaction	Hydrochemical indicators and source interaction
Singh et al. (2014)	Groundwater	Hydrochemical characterization and quality appraisal
Pandey & Kumar (2015)	Surface water	Spatial and temporal variability in an urban setting
Batabyal & Chakraborty (2015)	Groundwater	Hydrogeochemistry integrated with WQI

Methodological gap and rationale. Many studies evaluate only one water source or emphasize either WQI or hydrochemistry. A compact comparative design that applies the same analytical panel to surface water and groundwater allows differences to be attributed more directly to source type, while seasonal replication reduces the risk of interpreting a single sampling event as representative.

Methodology

1. Study design and sampling framework

A comparative observational design is proposed. Ten surface-water sites (river, lake, reservoir or pond locations) and ten groundwater sites (bore wells or open wells) are selected within the same regional setting. Sampling is performed twice: once in the pre-monsoon period and once after the monsoon. This yields 40 primary samples (20 sites x 2 seasons). Where resources permit, laboratory analyses are conducted in duplicate or triplicate.

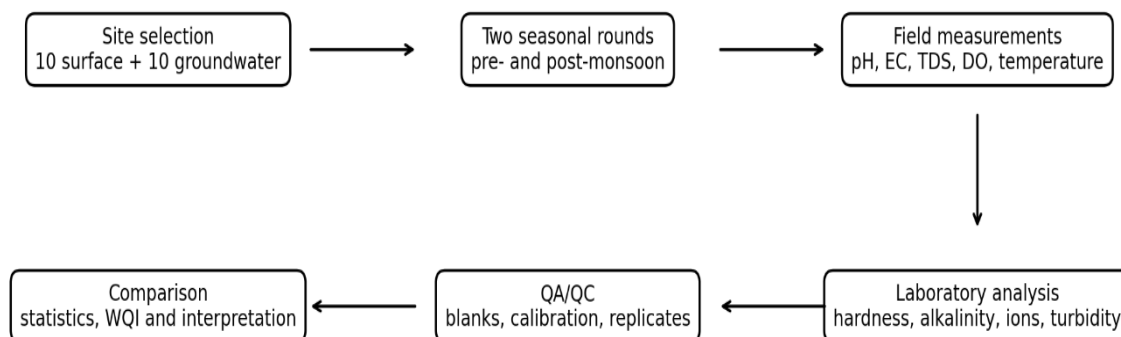
Table 2. Proposed Water Sampling and Quality Control Specifications

Component	Proposed specification
Surface-water sites	10 locations; collect 20-30 cm below the surface and away from immediate bank disturbance
Groundwater sites	10 wells; purge stagnant water for 5-10 min before collection
Sampling rounds	Pre-monsoon and post-monsoon
Container	1 L acid-washed HDPE bottle; separate bottle for DO when required
Preservation	Cool at about 4 C; analyze field-sensitive parameters immediately
Replicates / QA	Duplicate or triplicate analysis; blanks and calibration checks

2. Sample collection and preservation

All bottles are washed with laboratory detergent, rinsed with deionized water and finally rinsed with sample water at the site. Surface-water samples are collected below the surface to minimize floating debris. Groundwater is collected only after purging the well or outlet

sufficiently to obtain a representative aquifer sample. Samples are labeled with source type, site code, date, time and season. Field pH, EC, TDS, temperature and DO are measured immediately. Remaining samples are transported in an ice box and analyzed as soon as possible.

**Figure 1.** Proposed Water Quality Assessment and Analytical Workflow

3. Analytical parameters and methods

The same core analytical panel is used for both source types so that the comparison is internally

consistent. Parameters are selected because they represent acidity/alkalinity, dissolved mineral load, suspended matter, hardness and nutrient/anion contamination.

Table 3. Analytical Methods and Reporting Units for Physicochemical Water Quality Parameters

Parameter	Method / instrument	Reporting unit
Temperature	Portable thermometer / multiparameter meter	C
pH	Calibrated portable pH meter	pH units
EC	Conductivity meter	uS/cm
TDS	Meter or gravimetric confirmation	mg/L
Turbidity	Nephelometric method	NTU
Dissolved oxygen	DO meter / Winkler method	mg/L
Total alkalinity	Acid titration	mg/L as CaCO ₃
Total hardness	EDTA titration	mg/L as CaCO ₃
Calcium and magnesium	EDTA-based determination	mg/L
Chloride	Argentometric titration	mg/L
Sulphate	Turbidimetric method	mg/L
Nitrate	UV-visible spectrophotometry	mg/L
Fluoride	Ion-selective electrode / colorimetry	mg/L

4. Quality assurance and quality control

Meters are calibrated at the start of each sampling day using appropriate standards. Reagent blanks, duplicate samples and known

standards are included with each analytical batch. Glassware is rinsed with deionized water, and titrations are repeated when duplicate values differ excessively. For major-ion datasets, an ionic-balance check may be used where

sufficient ions are measured; a deviation within approximately $\pm 10\%$ is treated as acceptable for routine hydrochemical work. These controls reduce the risk that apparent differences between surface water and groundwater are analytical artifacts.

5. Data processing and statistical analysis

For each source type, mean, standard deviation, range and coefficient of variation are calculated. Pre-monsoon and post-monsoon observations are first summarized separately and then combined for source-wise comparison. If assumptions of normality and variance are reasonable, an independent-samples t-test is used to compare surface-water and groundwater means; otherwise, the Mann-Whitney test is preferred. Pearson or Spearman correlation can be used to identify associations such as EC-TDS, hardness-Ca/Mg and nitrate-chloride. A significance level of $p < 0.05$ is adopted for inferential tests.

6. Water Quality Index

A weighted arithmetic WQI is calculated from a selected set of comparable drinking-water parameters (for example pH, TDS, total hardness, alkalinity, chloride, sulphate, nitrate and fluoride). Each parameter is assigned a weight according to its relative importance, converted to a relative weight, and combined with the quality rating derived from the measured concentration and the corresponding guideline value. The final WQI provides a single comparative indicator, but individual parameters are retained because a

composite index can mask a specific exceedance. Similar WQI approaches have been used for groundwater and surface-water assessment by Balan et al. (2012), Ravikumar et al. (2013), Krishna Kumar et al. (2015) and Batabyal and Chakraborty (2015).

Step-by-step procedure

1. Select and code ten surface-water and ten groundwater locations within the same study region.
2. Collect pre-monsoon samples using clean HDPE bottles; measure field parameters immediately.
3. Transport preserved samples to the laboratory and complete titrimetric, spectrophotometric and ion-selective analyses.
4. Repeat the same protocol after the monsoon using the same sites wherever possible.
5. Apply QA/QC checks, compile source-wise and seasonal statistics, then calculate WQI.
6. Compare surface-water and groundwater patterns and interpret likely natural and anthropogenic controls.

Results

Important note: the following numerical values are an illustrative methodology-validation dataset created to demonstrate how the proposed analysis can be reported. They are not presented as real measurements from a field campaign.

Table 4. Comparative Physicochemical Characteristics of Surface Water and Groundwater

Parameter	Surface water (mean $\pm$ SD)	Groundwater (mean $\pm$ SD)	Illustrative interpretation
pH	7.42 $\pm$ 0.18	7.68 $\pm$ 0.22	Both near neutral to mildly alkaline
EC (μ S/cm)	540 $\pm$ 110	1010 $\pm$ 240	Higher dissolved ionic load in groundwater
TDS (mg/L)	345 $\pm$ 72	645 $\pm$ 155	Groundwater more mineralized
Turbidity (NTU)	4.8 $\pm$ 1.6	1.1 $\pm$ 0.6	Surface water more affected by suspended matter
Alkalinity (mg/L)	168 $\pm$ 35	276 $\pm$ 58	Greater bicarbonate buffering in groundwater
Hardness (mg/L)	142 $\pm$ 31	326 $\pm$ 74	Groundwater substantially harder
Chloride (mg/L)	48 $\pm$ 15	118 $\pm$ 36	Higher groundwater chloride burden
Sulphate (mg/L)	30 $\pm$ 10	62 $\pm$ 22	Higher groundwater mineral contribution
Nitrate (mg/L)	8.5 $\pm$ 3.1	21.0 $\pm$ 9.0	Groundwater shows greater nitrate accumulation
Fluoride (mg/L)	0.42 $\pm$ 0.10	0.79 $\pm$ 0.24	Geogenic contribution more evident in groundwater
DO (mg/L)	6.1 $\pm$ 0.8	4.2 $\pm$ 0.7	Surface water shows greater oxygen exchange

In the illustrative comparison, groundwater has higher EC, TDS, alkalinity, hardness, chloride, sulphate, nitrate and fluoride, whereas surface water has higher turbidity and DO. The pattern is consistent with the conceptual difference between longer subsurface residence/mineral dissolution and direct surface exposure. Similar groundwater mineralization patterns have been described by Rajankar et al. (2011), Dudeja et al. (2011), Sajil Kumar and James (2013) and Singh et al. (2014), while surface-water sensitivity to catchment pressure is consistent with Chandra et al. (2011) and Pandey and Kumar (2015).

For demonstration, a chemical WQI calculated from the illustrative dataset would classify the average surface-water condition as better than the average groundwater condition, largely because of the higher TDS, hardness and nitrate in the groundwater. This should not be interpreted as a universal rule: local geology, wastewater inputs, agricultural return flow and treatment status may reverse the pattern at particular sites. Elangovan and Dharmendirakumar (2013) also showed that groundwater adjacent to a polluted river corridor can reflect strong anthropogenic influence, while Brindha et al. (2014) showed that surface-water-groundwater interaction complicates simple source classification.

Conclusion and Discussion

The proposed methodology provides a practical framework for comparing physicochemical quality of surface water and groundwater using identical sampling periods, common analytical methods and source-wise statistics. The design emphasizes parameters that respond differently to surface processes and subsurface geochemistry. Groundwater is expected to show stronger mineralization signals such as EC, TDS, hardness and major-ion enrichment, whereas surface water is generally more exposed to turbidity, oxygen fluctuation and episodic runoff. However, the direction and magnitude of differences must be established empirically for each study area. The main methodological strengths are paired seasonal coverage, common analytical procedures, explicit QA/QC and the combined use of individual parameter interpretation with WQI. A limitation is that two seasonal rounds cannot capture all short-term events; future work should include monthly sampling, microbiological parameters, trace metals and GIS-based spatial analysis when resources permit. The literature up to 2015 supports continued integration of

hydrochemistry, statistical analysis and WQI rather than reliance on a single indicator.

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