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Hydrochemical Characterization and Water Quality Assessment of Pre-monsoon Samples Using EWQI, Ionic Facies Analysis, and Correlation Statistics

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Abstract

The present article focuses on the hydrochemical assessment of the water samples collected from various location within the study area in order to analyse their physicochemical properties along with the geochemical processes governing them. The Entropy- weighted Water Quality Index (EWQI) was used to assess the water quality after the quantification of main ions and trace constituents using standard analytical techniques. EWQI categorized 15% sample as extremely poor, 17.5% as poor, 40% as average, 25% as good, and only 2.5% as excellent. Gibbs plot was used to determine the mechanism controlling water chemistry, whereas Piper and Durov diagrams were used to compare hydrogeochemical facies and ionic development. The results obtained reveals that the water chemistry is controlled dominantly by the rock-water interaction and is characterised by alkaline nature with moderate to high mineralisation. Pearson correlation was carried out to understand the statistical relationship between the parameters. It clearly indicated that Electrical conductivity has a strong positive relationship with major cations and anions, whereas the trace elements, like arsenic, show weak to moderate correlations with major ions that suggests local and source specific controls on their distribution. A detailed understanding of the state of water quality and the mechanisms affecting solute accumulation before monsoon recharge is provided by the combined hydrogeochemical and statistical method. Moreover, the water quality of the study area needs to be taken into consideration as early as possible since the samples majorly falls in the average category of EWQI.

Keywords: Water quality assessment, Physico-chemical parameters, Piper, Durov, Gibbs, Correlation analysis, Entropy-weighted Water Quality Index.

1. Introduction

Water is crucial for human health, well-being, food security, and socioeconomic advancement (Ayoko et al., 2007; Patel et al., 2023; Patil et al., 2010). An estimated 97% of the world's water is salty, with freshwater making up the remaining 3%, just 0.01% of this 3% can be used by humans (Saeed et al., 2021). Therefore, in many parts of the world, especially in developing nations where many people are located far from a source of safe drinking water, the presence of toxins in natural freshwater remains one of the most significant environmental challenges (Ayoko et al., 2007; Kaur et al., 2021). Nonetheless, the issue of a supply of drinkable water is a worldwide one (Ayoko et al., 2007; Kumar et al., 2022).

Owing to population increase, agriculture, urbanisation, and industrialisation, many of the world's major rivers and groundwater supplies are either stressed or contaminated (Alam & Singh, 2023; Shanmugam, 2015; Soceanu et al., 2021). The fact is that humans use surface and groundwater resources for drinking, farming, and other uses, yet anthropogenic actions throughout these water uses have made these supplies less portable (Ahmed et al., 2023; Ayoko et al., 2007). Additionally, the world's population is struggling with a shortage of safe drinking water and the depletion of available water resources as a result of people's over-involvement in the natural processing of water resources (Ahmed et al., 2023). Although every city has a unique story, the primary causes of the water crisis are similar and include rising demand, zonal differences in water supply distribution, a lack of an ethical framework, a lack of resources and knowledge, significant changes in land use, long-term drops in water levels, pollution, and an increase in salinity (Kumar et al., 2022; Shanmugam, 2015).

Moreover, numerous contaminants, which can be found naturally in water or mixed in through the dumping of badly handled waste materials, affect the quality of water (Ahmed et al., 2023; R, 2021). Few contaminants are dissolved in water as water flows from one location to another as surface runoff, and even few are released directly into water bodies (Ahmed et al., 2023). Furthermore, there are numerous sources of contamination or sources that produce various pollutants, including household, agricultural, and industrial waste (Ahmed et al., 2023; Ashiyani, 2015). When water moves from one location to another, contaminants from sludge, industrial waste, sewage water, and agricultural fertilisers dissolve in the water. Likewise, the disposal of solid wastes, including sewage sludge and other toxic wastes, puts groundwater quality at risk because they seep into the groundwater (Ahmed et al., 2023).

Therefore, it is crucial to monitor water quality levels in order to determine pollution levels and potential environmental risks (Ashiyani, 2015). There is significant variation in the amounts of pollutants from various sample locations and environmental stages, necessitating

careful analysis and interpretation. Besides, a number of physico-chemical factors influence water quality, in order to predict, rate, or identify patterns in the water quality. Hence, it is becoming steadily more desired to get accurate water quality assessments that may be utilised for managing water resources and evaluating policy options to support industrial expansion, food security, and human well-being (Ayoko et al., 2007).

In light of the aforementioned contamination factors, this research article based on the data collected of various physico-chemical characteristics of few surface water as well as groundwater provides an interpretation. Compared to conventional Water Quality Indices (WQIs), the Entropy-Weighted Water Quality Index (EWQI), which gives weights to variables based on their variability and information entropy, was used to objectively assess the overall quality of the water based on the results obtained from the physico-chemical tests. The EWQI, which minimises human bias by deriving parameter weights from intrinsic variability, provides an information-theoretic alternative to WQIs, which are frequently constrained by subjectivity in assigning weights. To further comprehend the various characteristics, a correlation analysis was performed to determine the relationship between the measured water quality metrics which is even suggested by (Abinandan et al., 2014).

In broad terms, the data reported here would greatly advance our understanding of water quality in the rapidly evolving Saraikela-Kharsawan and East Singhbhum district of Jharkhand, in order to more effectively protect, preserve, and manage water resources.

2. Materials and Methods

2.1. Study Area

The geographical location of the study area (Figure 1) inside the Singhbhum Craton and includes portions of the East Singhbhum and Saraikela-Kharsawan districts in southeast Jharkhand (22.77°-22.86° N; 86.04°-86.31° E). The region has a tropical monsoon climate, with hot, dry summers (40-45°C), chilly winters (~8°C), and 1200-1400 mm of annual rainfall, mostly from the southwest monsoon (June-September). Geologically, it is distinguished by a significant thrust and shear zone that divides the highly metamorphosed northern rocks from the less metamorphosed southern terrain. Thin alluvium covers gneissic complexes, Rajmahal traps, and Gondwana formations. The main drainage system is made up of the Subarnarekha and Kharkai rivers, which exhibit North-west-South-east and South-west-South-east tendencies controlled by structural elements including foliation and joints. The underlying lithology and tectonic framework have an impact on the phreatic to semi-confined circumstances in which groundwater is found (CGWB; REDDY, 2013; Toppo, n.d.).

2.2. Methodology Adopted

Three main parts of the approach used in this study-field research, experimental analysis, and modelling-are depicted in Figure 2. During the pre-monsoon season, site surveying and sample collection were part of the field study. EWQI assessment, hydrochemical facies analysis (Piper, Durov, and Gibbs diagrams), and statistical evaluation using Pearson correlation were among the modelling and interpretative methods used in the experimental investigation, which involved the physicochemical measurement of water quality indicators.

2.3.1. Sampling and physico-chemical quantification

A total of 40 water samples (groundwater from wells, bore well and hand pumps, and surface water from lakes, ponds and rivers) were collected during the pre-monsoon season in May 2025. Standard sampling protocols were followed for sample collection. Sterile-cleaned high-density polyethylene containers, pre-treated with distilled water, capable of taking up to 1L of water, equipped with screw caps were used for sample collection. Total dissolved solids (TDS), pH, temperature, and electrical conductivity (EC) were assessed in-situ using portable multi-parameter meters of Lovibond SensoDirect 150 Set. Samples were transported in an ice box to the laboratory of IIT (ISM), Dhanbad for further testing. Water samples were examined using the standard procedure outlined in the comprehensive handbook “Standard Methods for the Examination of Water and Wastewater,” which was published by the Water Environment Federation (WEF), the American Public Health Association (APHA), and the American Water Works Association (AWWA). The standard method of two-point acid titration was used to determine carbonate, bicarbonate, total hardness (TH), and alkalinity in water. Whereas sulphate, fluoride, phosphate and nitrate concentration were determined using UV 3200 Touch Screen UV-Vis spectrophotometer of LABINDIA Analytical following the standard protocols. Chloride and potassium, levels in water samples were determined using Fisherbrand Accumet AB250 Ion Selective Electrode. Supplementary parameters like calcium, magnesium, sodium, aluminium, manganese, iron and aluminium were analysed using ICP-OES of iCAP 7400 Duo model. The results obtained were then compared against the water quality guidelines stated by the World Health Organisation (WHO) and BIS (IS 10500:2012) drinking water standards.

2.3.2. Entropy-Weighted Water Quality Index (EWQI)

The underlying idea of EWQI is to use the entropy value to determine the evaluation index's weight and to convert a substantial measure of water quality data into a symbolic value that precisely represents the state of the water quality (Li et al., 2021; Xiao et al., 2022). The entropy approach can successfully remove human influences from the weight calculation and has a high degree of objectivity (Egbueri et al., 2020; Xiao et al., 2022).

As a result, EWQI makes more sense than the traditional water quality index approach (Egbueri et al., 2020).

The calculation methods of EWQI comprises of the following five steps:

- a) Establish an initial water quality matrix
- b) Standardize data
- c) Determine the weight
- d) Determine quantitative standards of grading
- e) Determine the water quality index's entropy weight (Egbueri et al., 2020; Gautam et al., 2022).

On the crux of these, classification of water quality is done.

Firstly, the evaluation matrix (A) was associated with water quality data for “m” water samples and “n” chemical parameters during the first step (Equation 1).

$$A = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ a_{m1} & a_{m2} & \dots & a_{mn} \end{bmatrix} \quad (1)$$

The matrix (A) was altered into a standard-grade matrix (B) in the subsequent stage, using Equations 2 and 3.

$$b_{ij} = \frac{a_{ij} - (a_{ij})_{\min}}{(a_{ij})_{\max} - (a_{ij})_{\min}} \quad (2)$$

$$B = \begin{bmatrix} b_{11} & b_{12} & \dots & b_{1n} \\ b_{21} & b_{22} & \dots & b_{2n} \\ b_{m1} & b_{m2} & \dots & b_{mn} \end{bmatrix} \quad (3)$$

In the third step, the information entropy (e_j) was computed using Equations 4 and 5.

$$e_j = -\frac{1}{\ln m} \sum_{i=1}^m P_{ij} \ln P_{ij} \quad (4)$$

$$P_{ij} = \frac{(1+b_{ij})}{\sum_{i=1}^m (1+b_{ij})} \quad (5)$$

In the next phase, the weight of entropy (w_j) and the quality rating scale (q_j) were determined using Equations 6 and 7.

$$w_j = \frac{(1-e_j)}{\sum_{i=1}^m (1-e_j)} \quad (6)$$

$$q_j = \frac{C_j}{S_j} \times 100 \quad (7)$$

WHO (2011) and BIS (2012) define S_j as the standard intended limit of the chemical parameter (j) expressed in mg/L and C_j as the chemical parameter (j) content (mg/L). Subsequently, Equation 8 was used to determine EWQI.

$$EWQI = \sum_{j=1}^m w_j q_j \quad (8)$$

The measured water quality was categorised using the international standard in order to gain a better insight of the change in water quality. EWQI value ranging from < 50, 50-100, 100-150, 150- 200 and >200, which is divided into five grades: excellent (1), good (2), average (3), poor (4) and extremely poor (5) respectively (Han et al., 2024; Xia & Zeng, 2022). After calculating the EWQI, to better understand the water quality in the study area, the spatial distribution of water quality was mapped on the basis of the calculated EWQI value and GIS (Li et al., 2021), using Inverse Distance Weighting (IDW) to know the values of the unsampled location from known locations in Q-GIS software version 3.34.11. IDW is used because it is showing the best result in comparison to other interpolation techniques.

2.3.3. Hydrogeochemical Classification

Hydrogeochemical facies characterization of the water is governed by the Piper plot, Durov diagram and Gibbs Diagram (Şener et al., 2017; Singh et al., 2023). The percentages of ions (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , HCO_3^- , CO_3^{2-} , SO_4^{2-} , and Cl^-) are displayed in a trilinear diagram called a Piper diagram, which aids in characterising the geochemical evolution of water, in order to determine the alteration in the chemical nature of water that takes place. Three separate fields make up this diagram: a diamond-shaped field in the middle of the top side of the two triangle fields on the bottom is used to plot the water's overall chemical quality, while two triangle fields on the bottom side are used to plot cations (left) and anions (right). This graphic shows the relationships between big sample groups as well as the similarities and differences between water samples (Subba Rao et al., 2019, 2020). Whereas the expanded version of the Durov Diagram incorporates pH and TDS (mg/L) data to enable additional comparisons. A binary plot of total cation vs. total anion concentrations is formed by the sides of the Durov Diagram, a composite plot consisting of two ternary diagrams with the cations of interest plotted against the anions of interest (the data is normalised to 100%, as in piper). The Durov diagram's primary goals are to group data points that represent samples with comparable chemical compositions and to highlight practical relationships and characteristics for sizable sample groupings (Obeidat & Rimawi, 2017; Ravikumar, P, Somashekar, R.K Prakash, 2015). The anion ratio [$Cl^- / (Cl^- + HCO_3^-)$] and cation ratio [$Na^+ / (Na^+ + Ca^{2+})$] were plotted against TDS [where the TDS < 100 (mg/L), 100 to 1,000 (mg/L), and >1,000 (mg/L)] in Gibbs diagrams to differentiate the effects of rainfall, rock–water interactions, and evaporation processes as mechanisms governing the chemistry of water (Madhav et al., 2021; Subba Rao et al., 2019).

The Piper trilinear plot, Durov diagram and Gibbs diagram were made using Origin 2026 software.

2.3.4. Statistical Analysis

Furthermore, statistical research, including Pearson correlation -a frequently utilised statistic to evaluate the degree to which two variables are connected- was performed to look into the correlations between parameters and identify the major geochemical processes (Subba Rao et al., 2019). It is a simple statistic to determine how one factor affects another (Saeed et al., 2021). The mathematical relationship between the different water quality features of the samples were determined by using Pearson's correlation coefficient in order to compute correlation coefficients as described in Equation 9 (Chavan & Zambare, 2014).

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (9)$$

3. Results and Discussion

3.1. Physiochemical Quantification

The physico-chemical analysis of the pre-monsoon water samples indicated that the pH values varied from near-neutral to highly alkaline, similar to that shown in the study conducted by (Gawle et al., 2021), signifying a chemically buffered system throughout the pre-monsoon phase which is also reported in the research work conducted by (Rani et al., 2021). EC and TDS showed a lot of variation between samples. Review by (Rusydi, 2018) supports this stating that this is probably because of different dissolved ionic loads that may be affected by evaporation, source-specific inputs, and mineral-water interactions that remain prevalent during the dry season. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) dominated the major cation chemistry, followed by potassium (K^+) and sodium (Na^+). Varying TH classifies samples from being in moderate hard to hard categories. Bicarbonate (HCO_3^-) dominance prevailed in most of the samples among anion category highlighting the role of carbonic acid-mediated weathering, whereas chloride (Cl^-) and sulphate (SO_4^{2-}) showed noticeable variability. In trace metals, Iron (Fe) and manganese (Mn) contents differed among samples, with some surpassing suggested guideline range. Considerable variation in the levels of arsenic (As) was found among the samples. Few samples surpassed the acceptable limit guideline for drinking water. Presence of elevated arsenic indicates increased mobilisation during pre-monsoon geochemical conditions, especially in samples with greater TDS and alkaline pH. This type of enrichment can be related to desorption from iron-bearing phases, mineral dissolution, or prolonged water-rock contact at lower dilution conditions.

3.1.1. Entropy-Weighted Water Quality Index (EWQI)

A thorough evaluation of area water safety has been achieved by the EWQI calculations. Based on the EWQI values obtained, spatial distribution within the study area was done which can be seen in Figure 3. The EWQI values obtained of the samples ranges from 42 to >430. It has been categorised as excellent to extremely low quality (Figure 4). Only one sample fell under the “Excellent” quality category. About one-quarter of samples were classified “Good” many being less densely populated areas which we can be concluded based on the basis of the land use land cover of the study area stated in the reports of Central Ground Water Board (CGWB; REDDY, 2013; Toppo, n.d.). In the south and southeast, residential and rural areas, 40% of total samples, showed an “Average” EWQI, indicating a combination of anthropogenic and natural influences similar to that found in the study by (Unigwe & Egbueri, 2023). About 17.5% of the region has “Poor” water quality, especially in peri-urban and industrial areas. Six samples (15%) were ranked “Extremely Poor” echoing hotspot findings from spatial mapping that clearly signals water quality threats in industrial and old-settlement corridors (Table 1).

3.2. Hydrogeochemical Facies

In the present study, the water samples were classified hydro-geochemically using major cations and anions with conventional Piper trilinear plot, Durov diagram and Gibbs diagram. The Piper diagram (Figure 5) reveals similar result as mentioned in the work done by (Rani et al., 2021) that most water samples belong to the Ca–Mg–HCO₃ hydrochemical facies, as indicated by the dominance of Ca²⁺ and Mg²⁺ in the cation triangle and HCO₃⁻ + CO₃²⁻ in the anion triangle. The diamond field placed in the centre of the Piper diagram confirms the predominance of fresh, low-salinity water with an alkaline earth-bicarbonate type, which coincides with the finding stated by (Rani et al., 2021) and (Li et al., 2021), is mainly due to rock-water interaction.

These results are further supported by the Durov diagram (Figure 6), which combines conductivity, pH, and ionic composition. The majority of samples display near-neutral to slightly alkaline pH and low conductivity, indicating limited chemical formation and cluster around the Ca–Mg–HCO₃ field. This is in sync with the study of (Tajwar et al., 2025) indicating that carbonate weathering is the principal hydrochemical process. The lack of substantial Na⁺-Cl⁻ or SO₄²⁻ rich fields suggests that anthropogenic salinity, evaporite dissolution, and cation exchange are not significant processes in the waters that were analysed which we can comprehend by the results reported by (Tajwar et al., 2025) in their work before.

According to the Gibbs diagram (Figure 7), majority of examined water samples plot within the dominant field of rock–water interaction, with moderate TDS and comparatively low ratio

of $[\text{Cl}^-/(\text{Cl}^-+\text{HCO}_3^-)]$ and $[\text{Na}^+/(\text{Na}^++\text{Ca}^{2+})]$. This pattern of distribution indicates mineral dissolution activities, specifically carbonate and silicate weathering, are largely responsible for the sample's ionic composition. A small percentage of samples exhibit a modest inclination toward the evaporation dominance field, which could be explained by storage-related factors, surface water evaporation, or localised concentration effects similar to what is mentioned in the prior study conducted by (Li et al., 2021; & Shaikh et al., 2020).

Piper and Durov diagrams play complimentary roles in hydrochemical interpretation which can be seen by their comparative analysis. The Durov diagram conveys information regarding the geochemical processes and physicochemical circumstances, such as pH regulation and salinity evolution whereas the Piper diagram divides water samples specifically into hydrochemical facies according to main ion chemistry. The Gibbs diagram further backs the conclusion stating the predominance of Ca-Mg- HCO_3 type waters obtained from the prior two diagrams as this type of dominance is mainly seen due to rock-water interaction mechanism.

3.3. Correlation Analysis

The interrelationships between trace elements and physico-chemical properties of water samples were assessed using Pearson correlation analysis (Figure 8). A strong positive correlation between EC and TDS ($r=0.99$) was found which indicates that the EC is governed primarily by the concentration of dissolved ions and also that they are natural as well as of same origin as mentioned in the work of (Tajwar et al., 2025). EC and TDS are strongly correlated with Ca^{2+} , Mg^{2+} , SO_4^{2-} , and F^- ($r>0.65$) suggesting the role of alkaline earth metals and related ions in ionic strength and mineral dissolution in the particular sampling season. This is in line with the results obtained by (City et al., 2011; & Iqbal et al., 2023) in their work. Dominance of carbonate buffering system is reflected by strong positive correlation ($r=0.99$) between alkalinity and HCO_3^- . Similar result can be seen in the work of (Taofeek et al., 2019). Hardness is mainly controlled by the carbonate and silicate mineral dissolution, which becomes evident from the strong correlation of TH with Ca^{2+} ($r=0.96$) and Mg^{2+} ($r=0.86$). A similar result was reported in the work of (Ahmed et al., 2023 & Iqbal et al., 2023). Cl^- showed comparatively moderate relationships with major cations, suggesting localised or source-specific inputs rather than prevalent geogenic control as suggested in the study done by (Soceanu et al., 2021). A moderate positive correlation ranging from ($r=0.28$ to 0.39) of NO_3^- was observed with EC, TDS, Ca^{2+} , and Mg^{2+} . On the other hand, phosphate (PO_4^{3-}) showed primarily negative relationships with the majority of significant ions, suggesting that it comes from independent or man-made sources that are not directly related to mineral weathering processes. "As" showed weak correlations with alkalinity and bicarbonate ($r=0.11$ & 0.13), and a weak positive

association with iron ($r = 0.11$). There is absence of strong correlation between “As” and EC/TDS indicating that its mobilization is not only governed by salinity but also because of specific geochemical conditions. Manganese (Mn) has modest positive relationships with EC, TDS, Mg^{2+} , and SO_4^{2-} ($r = 0.38-0.49$).

Taking in consideration the above discussion, we can say that the correlation structure demonstrates how ion exchange inputs and mineral dissolution work together to affect the hydrochemical development of pre-monsoon water samples.

Overall, the Gibbs plots, multivariate statistical relationships, hydrochemical facies analysis (Piper and Durov diagrams), integrated evaluation of physico-chemical characteristics, and EWQI assessment all generally points that natural geochemical processes dominate the entire water chemistry and quality during the pre-monsoon period, with localised variations influenced by ionic enrichment and source-specific inputs.

4. Implications of the Study

The results of this study show how natural geochemical processes regulate ionic composition and overall water quality, offering significant insights into the pre-monsoon water chemistry across various water sources. When EWQI is used, complex water quality data may be communicated more easily, which aids in water use and monitoring strategy decision-making. Prior to the diluting effects caused by monsoon rains, seasonal baseline conditions can be better understood by using Piper, Durov, and Gibbs diagrams to identify dominating hydrochemical facies and geochemical controls. Even in waters that are mostly influenced by natural processes, the presence of arsenic, even though it has weak connections to main ions, emphasises the necessity of routinely monitoring trace elements. Taking all things into consideration, the integrated methodological approach used in this study can be successfully used for baseline assessment, comparative seasonal analysis, and sustainable water resource management in similar hydro-environmental contexts.

5. Conclusion

The main goal of the current study was to assess pre-monsoon water quality using the most realistic and robust EWQI method based on the results obtained from the physicochemical analysis. Hydrochemical diagrams, and statistical tools along with obtained EWQI result shows that the water chemistry is primarily controlled by natural geochemical processes, particularly rock-water interaction and ion exchange. The dominant role of geogenic controls over evaporative concentration is further supported by the interpretation of Gibbs plots. Major ions and salinity indicators exhibit substantial correlations with one another, according to Pearson correlation analysis, but arsenic exhibits a weak correlation with these parameters, suggesting

localised and condition-dependent mobilisation. The EWQI findings emphasise the need for source-specific assessment during the pre-monsoon phase by highlighting geographical diversity in water quality. This comprehensive evaluation offers a solid foundation for comprehending seasonal hydrochemical behaviour and a scientific foundation for upcoming monitoring and water quality control projects.

CRedit authorship contribution statement

Shilpy Kumari (SK): Conceptualization, Writing-original draft; Ankesh Kumar (AK): Literature search, Software and data curation; Vivek Kumar (VK): Methodology, Data curation; Ravi Prakash Kumar (RPK): Sample collection; Arunima Chakraborty (AC): Map making using Q-GIS; Ritesh Ranjan (RR): Experimental setup; Mamta (M): Testing; Khushboo Kumari (KK): Testing; Prasoon Kumar Singh (PKS): Conceptualization, Supervision, Resources, Review & Editing.

Declaration of competing interest

No conflicts of interest among authors to publish this manuscript.

Data availability

The study reported in the paper did not use any data.

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Declarations

Ethical Approval

This declaration is not applicable.

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Availability of data and materials

Due to continuing doctoral research, the datasets utilised in this study are not publicly available; however, the corresponding author may make them available upon reasonable request.

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