

"Social Transformation Through Dynamic Education"

Bharati Vidyapeeth's

Dr. Patangrao Kadam Mahavidyalaya, Sangli

Founder : Dr. Patangrao Kadam M.A., LL.B., Ph.D.

Principal Dr. D.G. Kanase M.Sc., Ph.D. (Affiliated to Shivaji University) P.O. Box No. 74, Sangli - 416 416 Ph. : 0233-2535229, Fax : 2535993 E-mail : bvpkc\_sangli@yahoo.co.in, dgkanase@gmail.com Website : www.dpkmsangli.bharatividyapeeth.edu



Accredited with 'B<sup>++</sup>' Grade by NAAC (3<sup>rd</sup> Cycle)

Ref. No. : BV/PKMS/ 21g /2022 -2023 To, The Principal, Anekant Education Society's, Jaysingpur College, Jaysingpur.

Subject: Regarding student exchange program under MoU

Respected Sir Madam.

Pursuant to the MoU signed between Anekant Education Society's Jaysingpur College Jaysingpur and Bharati Vidyapeeth's Patangrao Kadam Mahavidyalaya, Sangli. The Ph. D. student Burud Mahesh Dileep (NET-JRF) working under the guidance of Dr. A. R. Supale, Assistant professor P.G. Department of Chemistry Bharati Vidyapeeth's Patangrao Kadam Mahavidyalaya, Sangli. Interested in joining the student exchange program at DST-FIST Laboratory, Jaysingpur College Jaysingpur for research work under the guidance of Co-ordinator DST-FIST laboratory Dr. S. R. Sabale, Assistant Professor. Department of Chemistry Jaysingpur College Jaysingpur.

So, kindly request to you do needful.

Thanking you,

Yours faithfully,

(Dr.A. R. Supale) Asst. Professor in Chemistry

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Estd. - June 1964

Anekant Education Society's



# JAYSINGPUR COLLEGE, JAYSINGPUR

of Arts, Commerce, Science & Computer Science Jaysingpur - 416 101 Dist. Kolhapur, Maharashtra State, India AFFILIATED TO SHIVAJI UNIVERSITY, KOLHAPUR ACCREDITED AT THE 'A' LEVEL BY NAAC - UGC Tel. :- (O) 225381 Tel./Fax 226481(R) 225181-- ISD (0091) - STD (02322) website - <u>www.jaysingpurcollege.com</u> e-mail - jspcollegejsp@gmail.com

Ref. No. AES/JCJ/

Date: - 03/12/2021.

To, Dr. A. R. Supale, Department of Chemistry Dr. Patangrao Kadam Mahavidyalaya, Sangli wadi

Dear Sir,

You have worked as Inivted lecturer for M.Sc. -II, (Analytical chemistry) on the topic Theromodynamics in our college during the year 2021-22. We are very much thankful to you for sharing your academic excellence with our students. We expect the same kind of co-operation from you in future.

Thanking you in anticipation



Yours. 03 12/2021 Co-ordinator

M.Sc. (Analytical chemistry) M.Sc. Chemistry Jaysingpur College, Jaysingpur

Estd. - June 1964

Anekant Education Society's

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## JAYSINGPUR COLLEGE, JAYSINGPUR

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Ref. No. AES/JCJ/

Date: - 10 / 12 / 2021.

To, Dr. A. R. Supale, Department of Chemistry Dr. Patangrao Kadam Mahavidyalaya, Sangli wadi

Dear Sir,

You have worked as **Inivted lecturer** for M.Sc. -II, (Analytical chemistry) on the topic **Cyclic Voltametary** in our college during the year 2021-22.We are very much thankful to you for sharing your academic excellence with our students. We expect the same kind of co-operation from you in future.

Thanking you in anticipation

Yours.

M.Sc. (Analytical chemistry) M.Sc. Uhemistry Jaysingpur College, Jaysingpur



Founder Dr. Patangrao Kadam M. A., L. L. B., Ph. D.

Principal Dr. D. G. Kanase M. Sc., Ph. D. 'Social Transformation Through Dynamic Education'

Bharati Vidyapeeth's

Dr. Patangrao Kadam Mahavidyalaya, Sangli

(Arts, Science & Commerce College)

Affiliated to Shivaji University, Kolhapur.

Accredited with 'B''' Grade by NAAC, Bengaluru (CGPA 2.96)

DST-FIST Funded College (Level-0)

P. O. Box No. 74, Sangli- 416416. Phone: (0233) (O) 2535229, Tele. Fax.- 2535993 Email:-bvpkc\_sangli@yahoo.co.in, Website: http://dpkmsangli.bharatividyapeeth.edu

No.: B.V.D.P.K.M.S.

K.M.S. /2021-2022

Date: 31/05/2022

To, Dr. S. R. Sabale Department of Chemistry, Jaysinpur College, Jaysinpur.

Dear Sir.

We are very much thankful to you for working as Resource person to deliver guest lectures for M.Sc. 1 and II year class on topics 'Chromatographic Methods and Advanced Gas Chromatographic Techniques' respectively, during academic year, 2021-22.

Expecting the same co-operation in future.

Thanking you in anticipation.

Best Regards,

(Dr. A. R. Supale)

Co-ordinator, M.Sc. (Analytical Chemistry). Dr. Patangrao Kadam Mahavidyalaya, Sangli.

### Bharati Vidyapeeth's Dr. Patangrao Kadam Mahavidyalaya, Sangli

## Report on One day Seminar on 'Research Methodology' 18<sup>th</sup> May, 2022

The Seminar was jointly organized by Bharati Vidyapeeth's Dr. Patangrao Kadam Mahavidyalaya, Sangli and Jaysingpur College, Jaysingpur for B.Sc. and M.Sc. students on Wednesday, 18<sup>th</sup> May 2022. The main objective of this Seminar was to create awareness about basic terminologies of Research among the students. The Seminar was attended by faculty members and students from both colleges. The 102 participants were attended seminar through MS Team platform. (https://bit.ly/rmw2022)

Speaking on the occasion, Dr. A. R. Supale gave welcomes speech. Dr. R. S. Dhabbe introduced the Guest Speaker, Dr. S. D. Umdale (Asst. Professor in Botany, Jaysingpur College, Jaysingpur). Dr. Umdale, in his speech explained basic terminologies that are used in research. He also highlighted the importance of Research. He explained various methodologies that are used to carry out research. He also focused on referencing work and how to present research work. He briefed about the tools available to carry out the essential things. The session was followed by discussion. The speaker answered all the queries raised by students.

At the end Dr. S. R. Sabale concluded the seminar by delivering vote of thanks.

#### Some snaps of the online webinar:



1 | Page



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(Dr. A. R. Supale) Co-ordinator, IQAC Co-ordinator Internal Quality Assurance Coll Dr Patangrao Kadam Mahavidyalaya, Sangli.

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(Dr. D. G. Kanase) PRINCIPAL Dr. Patangarao Kadam Mahavidyalaya Sangli.-416416.(Sangliwadi.)

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Meeting Summary Total Number of Participants 102 Meeting Title Seminar On Research Methodology Meeting Start Time "5/18/2022, 8:22:03 AM" Meeting End Time "5/18/2022, 9:47:41 AM" Meeting Id a28df862-e01b-4323-9b5f-f4f96ce3cf97 Duration Email Role Participant ID (UPN) Full Name Join Time Leave Time "Bharati Vidyapeeth's Dr. Patangrao Kadam Mahavidyalaya, Sangli" "5/18/2022, 8:22:03 AM" "5/18/2022, 9:47:41 AM" 1h 25m bv.dpkms@bharatividyapeeth.edu Organizer bv.dpkms@bharatividyapeeth.edu "5/18/2022, 8:22:18 AM" "5/18/2022, 8:22:48 AM" 30s Attendee sagar mahindrakar Sandip (Guest) "5/18/2022, 8:22:18 AM" "5/18/2022, 9:46:59 AM" 1h 24m Presenter Saurabh Shirote "5/18/2022, 8:22:19 AM" "5/18/2022, 9:46:22 AM" 1h 24m Attendee Pratiksha Patil "5/18/2022, 8:25:12 AM" "5/18/2022, 9:47:16 AM" 1h 22m Attendee Shubham chougule "5/18/2022, 8:25:21 AM" "5/18/2022, 9:46:59 AM" 1h 21m Attendee mahesh patil "5/18/2022, 8:25:36 AM" "5/18/2022, 9:47:04 AM" 1h 21m Attendee Yash Vibhute "5/18/2022, 8:25:40 AM" "5/18/2022, 9:01:05 AM" 35m 25s Attendee satyam kore "5/18/2022, 8:25:53 AM" "5/18/2022, 9:06:49 AM" 40m 55s Attendee "5/18/2022, 8:27:07 AM" "5/18/2022, 9:47:41 AM" 1h 20m Attendee sagar mahindrakar "5/18/2022, 8:27:08 AM" "5/18/2022, 9:46:37 AM" 1h 19m Attendee Aman "5/18/2022, 8:27:24 AM" "5/18/2022, 9:47:41 AM" 1h 20m Attendee Maruti Pawar Nivati Bhojkar "5/18/2022, 8:27:29 AM" "5/18/2022, 9:47:41 AM" 1h 20m Attendee sanket "5/18/2022, 8:27:47 AM" "5/18/2022, 9:47:41 AM" 1h 19m Attendee Jineshwar chakote "5/18/2022, 8:27:59 AM" "5/18/2022, 8:39:32 AM" 11m 33s Attendee Dr. T. R. Lohar "5/18/2022, 8:28:29 AM" "5/18/2022, 9:47:10 AM" 1h 18m Attendee vrishabh magdum "5/18/2022, 8:28:44 AM" "5/18/2022, 9:47:41 AM" 1h 18m Attendee Prathmesh Sangale "5/18/2022, 8:29:36 AM" "5/18/2022, 9:47:41 AM" 1h 18m Attendee navjyot chavan "5/18/2022, 8:29:37 AM" "5/18/2022, 9:25:48 AM" 56m 11s Attendee Deepak Sidhappa Kamble "5/18/2022, 8:29:42 AM" "5/18/2022, 9:47:41 AM" 1h 17m Attendee Vishal More "5/18/2022, 8:30:03 AM" "5/18/2022, 9:47:41 AM" 1h 17m Attendee Nagesh Rajmane "5/18/2022, 8:30:10 AM" "5/18/2022, 9:34:34 AM" 1h 4m Attendee Shubham Phadtare "5/18/2022, 8:30:11 AM" "5/18/2022, 8:30:15 AM" 4s Attendee Shubham Phadtare "5/18/2022, 8:31:21 AM" "5/18/2022, 9:47:41 AM" 1h 16m Attendee

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Čo-ordinator Internal Quality Assurance Cell Dr Patangrao Kadam Mahavidyalaya. Sangli



Dr. Patangarao Kadam Mehavidyalaya Sangli.-416416.(Sangliwadi.)

Macromolecular Symposia

www.ms-journal.de

# Green synthesis of magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub> NPs) using *Acacia concinna* fruit extract and their antibacterial activity

Shubhangi Mane-Gavade, Arihant Malgave, Gurunath Nikam, Amruta Koli, Amit Supale, and Sandip Sabale\*

This paper describes green, simple, and efficient method for the synthesis of magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub> NPs) using *Acacia concinna* fruit extract for the first time. *A. concinna* fruit extract is used as reducing and stabilizing agent. Reduction of Fe<sup>3+</sup> ions by *A. concinna* fruit extract is examined by UV-visible absorption spectra (UV-Vis-NIR). To recognize the functional group responsible for Fe<sub>3</sub>O<sub>4</sub>, the NPs are characterized by Fourier transform infra-red spectroscopy (FTIR). The structural analysis of Fe<sub>3</sub>O<sub>4</sub> NPs is done by X-ray diffraction (XRD) which confirms cubic spinel structure and the average crystallite size of obtained NPs is found to be 28 nm. The morphological studies of Fe<sub>3</sub>O<sub>4</sub> NPs are done by scanning electron microscope (SEM) which depicts the quasi-spherical morphology. The green synthesized Fe<sub>3</sub>O<sub>4</sub> NPs shows distinctive antibacterial activities against gram-negative *E. coli* and *Pseudomonas aeruginosa* microorganism which confirms its potential in biomedical applications.

#### 1. Introduction

Magnetic nanoparticles (MNPs) have been attracting much attention because of their probable applications either as photocatalysis, ferro fluid technology, drug delivery, pigment, magnetic storage, magnetic ink printing, microwave absorption, biosensors, bio- separation, and in vivo drug delivery.<sup>[1,2]</sup> Particularly, magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>NPs) have attracted enormous interest, due to their unique magnetic properties, high electrical resistivity, and high chemical stability. It is often known that the activity of Fe<sub>3</sub>O<sub>4</sub>NPs strongly depends on their size, shape, and crystal phase.<sup>[3]</sup> Generally, the shape has a huge impact on the resulting properties of Fe<sub>3</sub>O<sub>4</sub>NPs and their potential applications.

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The ORCID identification number(s) for the author(s) of this article
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🕑 can be found under https://doi.org/10.1002/masy.202100140

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These potential applications of Fe<sub>2</sub>O<sub>4</sub>NPs have inspired the fast development of various synthetic techniques such as coprecipitation, hydrothermal treatment, spray pyrolysis, ultrasound irradiation, microwave-assisted method, and solvothermal method.<sup>[4,5]</sup> While, most of these methods rely on the use of toxic reducing agents and special equipment which make them less eco-friendly and costly. Hence, there is urgent need to develop environmentally benign methods, where, natural products could be used that are biocompatible, low cost, and easily available and one such method is the green synthesis.<sup>[6]</sup> It makes use of plant extracts that acts as an efficient reducing and capping agent in Fe<sub>3</sub>O<sub>4</sub> NPs synthesis. It is economic and valuable alternative with toxic free approach.<sup>[7]</sup> Many researchers reported the synthesis

of Fe<sub>3</sub>O<sub>4</sub>NPs using Artemisia annua,<sup>[8]</sup> leaf extract of Perilla frutescens,<sup>[9]</sup> Tridax procumbens,<sup>[10]</sup> and Caricaya papaya,<sup>[11]</sup> peel extract of plantain,<sup>[12]</sup> and also seed extract of grape proanthocyanidin.<sup>[13]</sup> However, no literature reports are available for the synthesis of Fe<sub>3</sub>O<sub>4</sub>NPsusing aqueous fruit extract of Acacia concinna.

In the present work, we report simple green route for the synthesis of magnetite NPs using *A. concinna* fruit extract. The phytochemicals present in *A. concinna* fruit extract are not only responsible for the formation of  $Fe_3O_4NPs$  but also act as capping agent for  $Fe_3O_4NPs$ . *A. concinna* is relatively large genus of plants belonging to *fabaceae* family<sup>[14]</sup>. The synthesized  $Fe_3O_4NPs$  were characterized using different characterization techniques and tested against pathogenic microorganisms.

#### 2. Result and Discussion

#### 2.1. Morphological and Structural Properties of Fe<sub>3</sub>O<sub>4</sub> NPs

Scanning electron microscope (SEM) was used to examine the surface morphology and structure obtained  $Fe_3O_4NPs$ . **Figure 1**A shows representative SEM images of  $Fe_3O_4$  NPs produced by *A*. *concinna* fruit extracts during the biosynthesis reaction. The morphology observed was quasi-spherical and several agglomerates can be appreciated. Various studies describe this agglomeration as a stearic effect caused by the interaction of the active sites of the

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Figure 1. SEM image spectra (A) and XRD spectra (B) of green synthesized Fe3O4 NPs.



Figure 2. UV-Vis spectral analysis (A) and FTIR spectra (B) of Fe<sub>3</sub>O<sub>4</sub>NPs.

NPs surface. However, the magnetic interaction generated by the individual  $Fe_3O_4NPs$  was considerate to explain this agglomeration by SEM.<sup>[15]</sup> The particle size of  $Fe_3O_4$  NPs was not possible to determine by SEM technique.

The phase compositions of prepared  $Fe_3O_4$  NPs were determined by X-ray diffraction (XRD) analysis. Figure 1B shows the XRD patterns of  $Fe_3O_4NPs$ . The XRD pattern of  $Fe_3O_4NPs$ exhibited peaks at  $2\theta$  of 35.78° along with other peaks 23.83°, 30.31°, 43.43°, 53.62°, 57.34°, 62.82°, 71.63°, and74. 39° fully indexed to diffraction from (311), (111), (220), (400), (422), (511), (440), (620), and (622) planes of magnetite phases. The sharp and strong diffraction peaks confirm the crystalline nature of  $Fe_3O_4NPs$  synthesized by *A. concinna* fruit extract. It was observed that the peaks of synthesized Fe<sub>3</sub>O<sub>4</sub>NPs were assigned to the cubic spinel phase of magnetic NPs. The XRD pattern was well matched with JCPDS card no. 01-075-0449.<sup>[16]</sup> The crystalline size of  $Fe_3O_4NPs$  was calculated from highest intensity peak using Scherrer's equation,

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$
(1)

where, D is crystallite size of Fe<sub>3</sub>O<sub>4</sub> NPs,  $\lambda$  is the wavelength of the X-ray source (0.1541 nm) used in XRD,  $\beta$  is the full width at half maximum of the diffraction peak. The average crystallite size for Fe<sub>3</sub>O<sub>4</sub>NPs was found to be 28 nm.

#### 2.2. Optical Properties of Fe<sub>3</sub>O<sub>4</sub>NPs

UV-Vis-NIR absorption spectra and FTIR spectra were used to determine the optical properties of Fe<sub>3</sub>O<sub>4</sub> NPs. The synthesized Fe<sub>3</sub>O<sub>4</sub>NPs were firstly characterized by UV-Vis-NIR absorption spectra as shown in **Figure 2**A. The UV-Visible spectrum of Fe<sub>3</sub>O<sub>4</sub> NPs shows a characteristic peak with a resultant absorption edge about 288 and 420 nm, which corresponds to Fe<sub>3</sub>O<sub>4</sub> NPs ground excitonic peak.<sup>[17]</sup> The synthesized Fe<sub>3</sub>O<sub>4</sub> NPs showed two absorption peaks, according to the literature.<sup>[4]</sup> The absence of other absorption peaks in the spectrum confirms the purity of the Fe<sub>3</sub>O<sub>4</sub> NPs.

The FT-IR spectra of  $Fe_3O_4$  NPs are shown in Figure 2B. The  $Fe_3O_4$  NPs showed high absorption peaks at 3428 and 3150 cm<sup>-1</sup>, indicating the presence of a primary amide group on the material's surface. Peak positions at 596 and 406 cm<sup>-1</sup> are due



Figure 3. Antibacterial activity of green synthesized Fe<sub>3</sub>O<sub>4</sub>NPs against *E. coli* and *P. aeruginosa*.

to specific Fe-O stretching and bending vibrations. The sharp medium intense peak at 1620.4 cm<sup>-1</sup> is assigned to -N-H bending and a small peak at 1123 cm<sup>-1</sup> is assigned to -C-N stretch. Other peaks at 1394 cm<sup>-1</sup>, 893 cm<sup>-1</sup> are due to the presence of bending of COO<sup>-</sup> groups, -C-H bend, respectively. FTIR data of Fe<sub>3</sub>O<sub>4</sub> materials confirm the presence of large and bulky bio-molecules.

#### 2.3. Antimicrobial Activity of Fe<sub>3</sub>O<sub>4</sub>NPs

Green synthesized magnetite NPs were analyzed for their antibacterial activity against *E. coli* and *P. aeruginosa* by Agar Well Diffusion Method. In this method petriplates containing 20 mL Muller Hinton medium were seeded with 34 h culture of bacterial strains. Wells were cut and Fe<sub>3</sub>O<sub>4</sub> NPs were added. The plates were then incubated at 37°C for 24 h. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well. Antibacterial activity of Fe<sub>3</sub>O<sub>4</sub> NPs against gram-negative bacteria was observed, indicating that these NPs are effective antibacterial agents. **Figure 3** shows antibacterial activity of green synthesized Fe<sub>3</sub>O<sub>4</sub>NPs against *E. coli* and *Pseudomonas aeruginosa*.

The mechanism of antibacterial activity of  $Fe_3O_4NPs$  on microorganisms is partially known.  $Fe_3O_4$  NPs may attach to the surface of the bacterial cell membrane via interacting with sulfur containing proteins, disturbing permeability and respiration functions of cell, resulting in cell kill.<sup>[18]</sup> It is also possible that  $Fe_3O_4$  NPs not only interact with the surface of the membrane, but can also penetrate inside the bacteria. The action of  $Fe_3O_4$ NPs on bacteria was also due to interaction with thiol groups (–SH) of proteins on the bacterial cell surface, resulting in cell lysis. It is important to remember that  $Fe_3O_4NPs$  do not harm all cells; however, with the right magnetic field, NPs can be used to kill *bacteria*.<sup>[19]</sup> A strong bactericidal activity was observed against *E. coli* and *P. aeruginosa*. The summarized results are shown in **Table 1**.

#### 3. Conclusion

Here we reported green synthesis of Fe<sub>3</sub>O<sub>4</sub>NPs using *A. concinna* fruit extract as an effective bio-resource. The concentration of

**Table 1.** Antibacterial activity of Fe<sub>3</sub>O<sub>4</sub> NPs.

Test organisms	Zone of inhibition (diameter in mm)								
	A. Concinna fruit extract	50 ppm Fe <sub>3</sub> O <sub>4</sub> NPs	100 ppm Fe <sub>3</sub> O <sub>4</sub> NPs						
Esherichia coli	0	12	20						
Pseudomonas aeruginosa	0	10	22						

A. concinna fruit played significant role in the formation of  $Fe_3O_4NPs$ . The formation of  $Fe_3O_4$  NPs was demonstrated by UV-Vis-NIR spectroscopy in the absorbance peak at 288 and 420 nm. Green synthesized  $Fe_3O_4$  NPs with bactericidal activity against *E. coli* and *P. aeruginosa was* demonstrated by Agar Well Diffusion method. Overall, the results obtained confirmed that the green synthesis of  $Fe_3O_4NPs$  using *A. concinna* fruit extract is simple, fast, cost-effective and environment friendly relative to physical and chemical methods and have promising application in the field of medicine and hygiene.

#### 4. Experimental Section

*Materials*: For the synthesis of NPs analytical research (AR) grade ferric chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O<sub>,</sub>99%) and ammonia was purchased from Sigma–Aldrich, India. All chemicals were used without further purification. *A. concinna* fruit was collected from *A. concinna* shrub. Distilled deionized water was used for preparing solutions prior to their use throughout the experiments.

Synthesis of  $Fe_3O_4NPs$ : Ferric chloride hexahydrate (FeCl<sub>3.</sub>6H<sub>2</sub>O) was added to aqueous fruit extract solution in the ratio 1:2 with constant stirring. The mixture was stirred for 1 h. The color of solution changes to yellowish to dark brown. Freshly prepared ammonia solution were added drop wise into it with constant stirring. The pH of the solution was adjusted to 9 and stirs the solution for 2 h. After completion the reaction, Fe<sub>3</sub>O<sub>4</sub> NPs was separated from magnet and washed several times with water. Dried the NPs and annealed at 400°C for 2 h. These prepared NPs are used for further characterizations.

Characterizations: The synthesized  $Fe_3O_4$  NPs were characterized using various analytical techniques. The reduction of the  $Fe^{3+}$  ions was monitored by measuring the absorbance of the reaction medium with

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UV-Vis-NIR spectrophotometer (V-777, Jasco, Japan). The XRD pattern of synthesized Fe<sub>3</sub>O<sub>4</sub> NPs was recorded on a Philips automated X-ray diffractometer (Model PW-3710) equipped with a crystal monochromator employing Cu-K $\alpha$  radiation of wavelength 1.5406 Å in 2 $\theta$  range from 20° to 80°. The FTIR spectra of Fe<sub>3</sub>O<sub>4</sub> NPs were recorded on FTIR-4600 (Jasco, Japan). The surface structures were examined using scanning electron microscopy (SEM, S4800, HITACHI Inc.).

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### **Keywords**

Acacia concinna fruit extract, antibacterial activity, characterization,  ${\rm Fe_3O_4NPs},$  green synthesis

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## Monitoring and Assessment of Water Quality using Multivariate Statistics of Physico-chemical Parameters to establish Baseline Level around proposed Jaitapur Nuclear Power Plant (JNPP), India

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#### Abstract

This study illustrates the usefulness of multivariate statistical techniques to provide straightforward data interpretation as well as valuable insights of datasets to get better information about the water quality and helps to design monitoring networks for effective management of available water resources. In this study, Multivariate statistical analysis, Cluster analysis, Principal Component Analysis, Factor Analysis, Water Quality Index and Piper diagram are used to analyze the water data and to prepare the baseline of water parameters around the proposed JNPP. Piper diagram indicates that the primary salinity ("non-carbonate alkali") exceeds 50 % which means that the chemical properties of water are dominated by alkalies and strong acids. Water quality indices indicate that water is non-polluted and fully fit for drinking purposes.

Principal component analysis and factor analysis applied for water parameters point towards the common source of minerals and high level of dissolved organic matter. Trace metal analysis shows significant but little participation of zinc, copper, nickel, iron and barium in water quality. The baseline developed and the data obtained will be useful for the water quality analysis after post-plant operation in this region.

**Keywords:** Water, JNPP Region, Physico-chemical parameters, Multivariate Statistics, Baseline.

#### Introduction

Safe water is a basic human right and pre-condition for health and development, yet it is still denied to millions of people of the developing world. Poor sanitation and hygiene coupled with insufficient safe water cause water-related diseases leading to 3.4 million deaths per year and most of them are children<sup>21,23</sup>. India in 1974 enacted 'The Water Act' for prevention and control of water pollution to maintain and restore purity of water in the country. The act was further amended in 1992 and 2003. Currently, India's environment has become fragile and is of concern because of increasing industrialization, urbanization and growth in population<sup>9</sup>. Water quality expresses the suitability of water to sustain various uses and processes. Every use or process requires certain physical, chemical and biological characteristics of water. Physical and chemical parameters of water are easily defined and hence, criteria set for water quality are largely based on physical and chemical conditions of the water. Biological methods of analyzing water quality are based on a diversity index derived from information theory. These indices express the relative importance of species, also they are dimensionless and independent of the sample size collected.

Once the water gets contaminated, it is difficult to restore its quality. Consequently, directly or indirectly everyone gets affected. Heavy metal contamination is a major problem in several communities and agricultural areas. Commercial agrochemicals, savage water and industrial wastewater are the measured sources of heavy metal contamination<sup>15,16,25</sup>. The contamination in an aquatic community is of major concern because of its toxicity, abundance and persistence in the environment. This may contaminate the aquatic ecosystem or public health<sup>4,22</sup>. Thus the analysis of water quality is important to preserve the environmental system.

The application of basic and multivariate statistical methods including Cluster analysis (CA), Principal Component Analysis (PCA), Factor Analysis (FA) and Water Quality Index (WQI) for the investigation of water quality data are widely found in literature<sup>2,3,8,24,26</sup>. Government has responded to the water findings by implementing required appropriate action plans at diverse locations<sup>6</sup>. Hence it is important to provide the detailed composition of water parameters to help the local environmental policymakers.

#### Study area

Jaitapur is a small village situated in the Rajapur Tehsil of Ratnagiri District, Maharashtra. It lies on the Arabian Sea coast. Nuclear Power Corporation of India Limited (NPCIL) proposed a Nuclear Power Plant with a 9900 MW capacity near Jaitapur. This project is located at 16.55° N; 73.35° E, a part of Konkan in the Western Ghats of Maharashtra. The issue was highlighted by different non-governmental organizations because of the adverse effects of radiation and different types of pollution. Also, many other industries like thermal power, mining of aluminium etc. are being constructed in this Konkan region. This Konkan region is famous for mango production and export especially Devagad alphanso, jackfruits, cashew and cashew nuts, rice, ragi, kokam fruits and other by-products. Hence it is necessary to study the hydrochemistry of this Konkan area. For our study, we have selected an area of about 30 km distance which covers Devagad and Rajapur Tehsil from Sindudurg and Ratnagiri district respectively.

The present study represents the variation in water quality parameters in different seasons. Physical, chemical and biological parameters were studied in different seasons (winter, summer and post-monsoon).

Our study will be helpful to assess the impact of these industries after their post operations. Hence this preoperational study has been undertaken which will play an important role in establishing the baseline level of water parameters.

#### **Material and Methods**

The basic aim of the proposed study was to carry out a comprehensive assessment of water samples to establish the baseline data on physico-chemical parameters and trace metals present in water around the proposed Jaitapur Nuclear Power Plant (JNPP) environment up to a distance of 30 km from the site. To fulfill this aim, we have prepared the sampling frame of all the villages within the territory of 30 km from JNPP. By using simple random sampling, 15 villages are selected as sampling positions and located using GPS positions (Table 1)<sup>12</sup>.

The base map (Fig. 1)<sup>18</sup> was prepared from these sampling locations. Water sampling from these selected locations was done by following the proper scientific methods with maximum standards for three seasons viz. winter, summer and post-monsoon. The water samples were tested for the

parameters like pH, Electrical conductivity (EC), Total Dissolved Solids (TDS), Hardness, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Turbidity, SAR, Maximum Probable Number (MPN), the concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. In addition, trace metals from water were analyzed in post-monsoon season using an inductively coupled plasma mass spectrometer (ICP/MS).

The obtained data is subjected to multivariate statistical analysis such as cluster analysis (CA), principal component analysis (PCA), factor analysis (FA), water quality index (WQI) and piper diagram used to express the water quality. CA is the technique to form meaningful groups of entities from a large number of variables called clusters. The resulting cluster possesses high internal homogeneity and high external heterogeneity<sup>5</sup>.

In the current study, the most common hierarchical clustering approach is adopted with Ward's method and squared Euclidian distance measure as a measure of similarity. This method uses the analysis of variance approach to evaluate the distance between two clusters. Factor analysis (FA) and principal component analysis (PCA) are data reduction techniques.

The main purpose of FA is to reduce the dimensionality of a dataset consisting of a large number of inter-related variables without losing the variability present in the dataset. PCA transforms the original set of variables into a new set of independent variables called principal components. Principal components are the linear combination of original variables. The purpose of FA can be achieved by applying varimax rotation to principal components obtained after applying PCA to normalized dataset<sup>19</sup>. New variables are termed as varifactors (VF).

S.N.	Locations	Name	GPS Posit	ion
1.	Devgad	S1	N- 16° 22'43.4"	E- 73° 24'02.9"
2.	Nadan	S2	N- 16° 26'29.0"	E- 73° 24'52.0"
3.	Baparde	S3	N- 16° 26'26.8"	E- 73° 28'34.8"
4.	Thakarwadi	S4	N- 16° 30'33.8"	E- 73° 22'19.2"
5.	Vijaydurg	S5	N- 16° 33'34.5"	E- 73° 20'05.3"
6.	Pural	S6	N- 16° 27'48.4"	E- 73° 23'04.0"
7.	Hatiwale	S7	N- 16° 35'40.9"	E- 73° 32'27.1"
8.	Ansure	S8	N- 16° 33'44.5"	E- 73° 24'27.0"
9.	Mithgawane	S9	N- 16° 35'06.5"	E- 73° 22'19.9"
10.	Madban	S10	N- 16° 25'47.1"	E- 73° 20'43.3"
11.	Jaitapur	S11	N- 16° 37'36.2"	E- 73° 38'17.8"
12.	Nate	S12	N- 16° 38'17.8"	E- 73° 21'25.2"
13.	Rajapur	S13	N- 16° 39'19.6"	E- 73° 30'47.1"
14.	Ambolgarh	S14	N- 16° 38'35.6"	E- 73° 19'44.8"
15.	Bhalawali	S15	N- 16° 43'24.1"	E- 73° 24'23.7"

 Table 1

 Sampling sites and their GPS positions<sup>15</sup>



Figure 1: Base map of JNPP and locations of soil sampling sites<sup>18</sup>

Water quality index (WQI) is also used to indicate the water quality<sup>7,10,11</sup>. Water quality index (WQI) is a singledimensional number calculated mathematically from large water quality data. WQI range is classified in part as: 0-30 as "excellent", 30-50 as "good", 50-60 as "moderate", 60-70 as "poor", 70-80 as "very poor" and 80-100 as "unfit for drinking"<sup>14</sup>. The water quality indexes calculated are based on 13 physico-chemical parameters using ICMR and ISI standards.

A piper diagram is used to visualize the hydrochemistry. It is a combination of two tri-linear plots, left represents anions and right represents cations and one diamond plot in the middle, representing the combination of both anions and cations<sup>17</sup>. For first left trilinear plot, take normalized concentrations of three anions on every three sides of a triangle and plot the points.

For a second, right trilinear plot takes normalized concentrations of three cations on every three sides of a triangle and plot the points. Now plot the line passing through anions point and parallel to outer axis of first triangle and a line passing through cations point and parallel to an outer axis of the second triangle. These pair of lines intersect in the diamond plot and project the anion and cation points. These three points represent one sample. Position of point in the diamond plot represents nature of water.

#### **Results and Discussion** Descriptive statistics

**General Descriptive Statistics of Water parameter:** The physicochemical characteristics along with the standard deviation, skewness, kurtosis and p-value of the Shapiro-wilk test of normality for winter, summer and post-monsoon seasons are presented in table  $2^{18}$ . The pH is determined to express the activity of the hydrogen ions [H<sup>+</sup>]. The pH range for normal water is 6.5- 8.5, acidic < 6.5, alkaline > 8.5.

From the results, it is observed that the pH values vary from 5.84 to 8.04, 5.63 to 7.20 and 6.11 to 7.05 (mean; 6.75, 6.49 and 6.60) for winter, summer and post-monsoon season respectively which are close to neutral while Kurtosis value shows flat nature. EC is directly proportional to the concentration of ions coming from dissolved salts, organic salts and inorganic material. EC value varies from 0.10 to

0.30, 0.07 to 0.82, 0.12 to 0.61 (mean; 0.18, 0.34, 0.23) for winter, summer and post-monsoon seasons respectively. In post-monsoon season, Kurtosis shows less variation from the mean value with normal nature.

TDS value varies from 166.40 to 241.30, 166.80 to 287.00 and 174.68 to 233.70 ppm (means: 195.53, 213.38 and 199.33 ppm) for winter, summer and post-monsoon season respectively. Like pH, TDS also shows flat positively skewed nature in all seasons. In post-monsoon season only, SW p-value for pH, EC and TDS shows normal behaviour.

The hardness of water is a natural characteristic that enhances the portability and consumers acceptability for drinking water. From the health studies, it is found that mortality rates due to heart diseases are negatively correlated with the hardness of the water.

For the current study, hardness varies from 100.00 to 170.00, 110.00 to 225.00 and 112.00 to 160.00 ppm (means: 126.67, 148.80 and 128.60 ppm) for winter, summer and post-monsoon seasons respectively. The result shows that water understudied region is moderately hard.

Table 2
Physico-chemical properties of Water samples of winter, summer and post-monsoon seasons from
15 villages near JNPP <sup>16</sup>

	pH	EC	TDS	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K+	HC O <sub>3</sub> ·	Cl	NO <sub>3</sub> <sup>-</sup>	<b>SO</b> <sub>4</sub> <sup>2</sup>	Hard ness	DO	BO D	CO D	Turbi dity	SAR	MP N
				WI	NTER SE	EASON		1								1		
Min	5.84	0.10	166. 40	3.50	0.28	22.6	0.12	2.20	1.70	2.80	20.9	100.0	6.0 0	2.88	24.0	1.50	11.36	1.00
Max	8.04	0.30	241.	7.75	1.70	55.8 8	0.51	5.00	4.50	7.28	33.4	170.0	11. 33	4.80	40.0	3.10	19.04	5.00
Mean	6.75	0.18	195. 53	5.67	1.07	29.3 7	0.34	3.72	3.18	4.60	27.7	126.6 7	7.8	4.14	34.4 7	2.28	15.00	2.87
SD	0.66	0.06	22.8	1.09	0.55	7.83	0.15	0.91	0.72	1.29	4.03	19.52	1.4 9	0.52	4.34	0.49	2.60	1.19
Skewne	0.55	0.57	0.58	-0.20	-0.30	3.08	-0.35	-0.27	0.01	0.55	-0.01	0.54	1.0 0	-0.75	-0.75	0.04	0.45	0.00
Kurtosi $s(\gamma_2)$	-0.46	-0.06	-0.61	0.07	-1.76	10.8 1	-1.20	-1.29	1.13	0.13	-1.36	0.14	0.7	1.06	1.06	-1.26	-1.34	- 0.79
SW P- Value	0.55	0.52	0.34	0.95	0.02	0.00	0.04	0.37	0.06	0.39	0.31	0.48	0.2	0.29	0.29	0.50	0.07	0.28
	1			SUN	IMER S	EASON		1								1		
Min	5.63	0.07	166. 80	4.85	0.59	21.3 2	0.16	3.50	1.10	2.31	20.6	110.0 0	6.4 0	3.00	25.0 0	1.30	10.50	1.00
Max	7.20	0.82	287. 00	7.51	2.31	36.2	0.61	6.10	4.20	5.12	30.1 6	225.0	8.2 0	5.70	48.0 0	2.80	19.20	4.00
Mean	6.49	0.34	213. 38	6.07	1.42	28.8 6	0.40	4.37	1.94	3.97	25.0 9	148.8	7.2 8	4.61	38.6 0	1.99	13.92	2.53
SD	0.43	0.23	35.8 8	0.78	0.48	4.42	0.15	0.76	0.90	0.78	2.94	35.26	0.5	0.74	6.10	0.40	2.54	0.83
Skewne	0.03	0.72	0.69	0.12	0.10	-0.02	0.21	0.78	1.27	-0.33	-0.02	0.80	0.3	-0.52	-0.58	0.36	0.73	0.31
Kurtosi s(γ <sub>2</sub> )	-0.10	0.10	-0.34	-0.44	-0.29	-0.34	-0.97	0.05	1.20	0.01	-1.05	-0.15	- 0.3	0.14	0.44	-0.02	0.18	0.23
SW P- Value	0.72	0.21	0.38	0.78	0.97	0.51	0.13	0.12	0.01	0.85	0.51	0.15	0.5	0.79	0.77	0.89	0.36	0.03
	1			PO	ST-MON SEASC	ISOON N		1								1		
Min	6.11	0.12	174. 68	4.75	1.00	20.5 0	0.15	3.10	1.12	1.18	21.2 0	112.0 0	5.2 3	3.00	25.0 0	1.80	1.20	1.00
Max	7.05	0.61	233. 70	7.18	2.16	38.5 0	0.60	5.80	4.00	5.90	34.1 2	160.0 0	6.5 9	5.80	48.0 0	3.00	18.20	4.00
Mean	6.60	0.23	199. 33	6.12	1.48	27.9 7	0.38	4.31	2.99	4.45	28.4 1	128.6 0	5.9 4	4.56	37.3 3	2.31	14.74	2.80
SD	0.37	0.12	22.6 1	0.87	0.41	4.11	0.15	0.83	0.81	1.23	3.20	17.22	0.3 8	0.98	7.31	0.40	4.31	0.86
Skewne $ss(\gamma_1)$	-0.10	2.51	0.62	-0.27	0.47	0.90	-0.17	0.00	-0.59	-1.66	-0.49	1.04	- 0.5 5	-0.42	-0.49	0.68	-2.38	- 0.34
Kurtosi s(γ <sub>2</sub> )	-1.87	7.89	-1.36	-1.60	-1.03	2.45	-1.41	-0.92	0.50	2.65	0.71	-0.62	- 0.0 6	-1.20	-0.95	-0.64	7.17	- 0.11
SW P- Value	0.01	0.00	0.01	0.05	0.12	0.30	0.24	0.54	0.21	0.00	0.77	0.00	0.3 9	0.11	0.25	0.08	0.00	0.05

Note: Bold value represents significant p-values

DO is of prime importance for aquatic life and shows an inverse relation with water temperature. DO value varies from 6.00 to 11.33, 6.40 to 8.20 and 5.23 to 6.59 ppm (means: 7.83, 7.28 and 5.94) for winter, summer and postmonsoon seasons respectively. BOD is the amount of oxygen required by bacteria to stabilize decomposable organic matter<sup>24</sup>. BOD does not have direct health implications but is an important parameter for defining overall water quality. BOD values vary from 2.88 to 4.80, 3.00 to 5.70 and 3.00 to 5.80 ppm (means: 4.14, 4.61 and 4.56 ppm) for winter, summer and post-monsoon seasons respectively.

COD also does not have hazardous implications but is helpful in indicating toxic conditions. COD is a measure of water equivalent to the requirement of oxidizing organic matter contents in the presence of the strong chemical agent. COD value varies from 24.00 to 40.00, 25.00 to 48.00 and 25.00 to 48.00 ppm (means: 34.47, 38.60 and 37.33 ppm) for winter, summer and post-monsoon seasons respectively. BOD and COD both are negatively skewed in all seasons: flat nature in the post-monsoon season and peaked in other seasons. Turbidity in water arises due to the presence of very finely divided solids which are not filterable by routine methods.

Turbidity has direct health effects depending on the composition of turbidity causing materials. Turbidity values vary from 1.50 to 3.10, 1.30 to 2.80 and 1.80 to 3.00 NTU (means: 2.28, 1.99 and 2.31 NTU) for winter, summer and post-monsoon seasons. A maximum permissible limit of turbidity is 4 NTU. All the turbidity values are within permissible limits and show flat nature. The sodium adsorption ratio (SAR) measures the suitability of water for irrigation. SAR is determined by using the concentration of solids dissolved in water. SAR values vary from 11.36 to 19.04, 10.50 to 19.20 and 1.20 to 18.20 (means: 15.00, 13.92 and 14.74) for winter, summer and post-monsoon seasons respectively. Most probable number (MPN) is found to be 3 for the maximum number of sample sites in all seasons.

General descriptive statistics of trace metals concentration: All locations show high concentration of Iron (Fe) (mean 205.97 ppb). The maximum permissible limit for drinking water is 200 ppb; half of the locations exceed the limit. Iron is present in soil and rocks in an insoluble form, but many complex reactions take place in nature which may give rise to many soluble forms of iron. These soluble forms are present in water passing through such formations. Severe problems may rise if drinking water supplied contains a high concentration of iron. The standard statistical analysis is carried out to describe the heavy metal contents in water and is given in table 3.

The concentration of chromium (Cr), Cobalt (Co) and cadmium (Cd) for all sample sites and concentration of Arsenic (As) for three sampling sites are below detection level. The highest value of 'As' is found to be 3.545 ppb with a mean concentration 2.485 ppb. All the values are well below the permissible limit. After Fe, Ba concentration in water is significant with mean 191.3 ppb and the maximum value observed is 263.1 ppb. The average concentration of heavy metals studied in decreasing order as Fe, Ba, Mn, Cu, Pb, Mn, As and Ni was found to be 502.97, 191.3, 72.261, 16.398, 4.685, 4.069, 2.485 and 2.277 ppb respectively. Except As and Ba, all other heavy metals show positively skewed behaviour. Except for Mn, Cu and Zn, all other heavy metals show flat nature. Also, SW p-values confirm that only Cu and Mn are normally distributed.

**Paired t-test analysis:** The change in the mean behaviour of the water parameter is analyzed with the help of paired t-test and is presented in table 4. EC changes significantly (p-value, 0.031) in winter to summer season change. The hardness of water increases significantly (p-value, 0.030) in winter to summer season change and drops down significantly (p-value, 0.033) in summer to post-monsoon season change to match with mean behaviour in winter season. The DO decreases significantly in summer to post-monsoon (p-value, 0.000) and winter to next post-monsoon (p-value, 0.000) season changes.

	Mn	Fe	Ni	Cu	Zn	As	Pb	Ba
Parameters			- 1-	0		120	- ~	2.
N of cases	15	15	15	15	15	12	12	12
Minimum	1.010	134.600	1.006	5.834	35.200	1.231	1.020	112.470
Maximum	13.360	318.450	4.638	71.340	123.300	3.545	10.270	233.450
Mean	4.069	205.970	2.277	16.398	72.261	2.485	4.400	183.527
Standard Deviation	3.302	61.503	1.194	15.969	21.356	0.752	3.175	42.267
Skewness(y1)	1.811	0.466	0.819	3.285	0.640	-0.212	0.728	-0.496
Kurtosis( $\gamma_2$ )	3.655	-1.209	-0.485	11.702	1.487	-0.657	-1.018	-1.056
SW Statistic	0.814	0.909	0.887	0.563	0.958	0.937	0.867	0.909
SW P-Value	0.006	0.132	0.060	0.000	0.656	0.460	0.060	0.207

 Table 3

 Basic descriptive statistics of trace metal analysis of water samples from 15 villages near JNPP

Note: Bold value represents significant p-values

The BOD (p-value, 0.043) increases significantly in winter to summer season change. Turbidity shows a significant increase in summer to post-monsoon (p-value, 0.035) season change. The mean concentration of Ca changes significantly (p-value, 0.021) in winter to the next post-monsoon season change. The mean concentration of Mg changes significantly in winter to summer (p-value, 0.043) and winter to next postmonsoon (p-value, 0.006) season change. K concentration shows a significant increase (p-value, 0.009) in winter to summer and a significant decrease (p-value, 0.003) in winter to next post-monsoon season change.

Cl<sup>-</sup> concentration shows a significant decrease (p-value, 0.000) in winter to summer and significant increase (p-value, 0.000) in summer to post-monsoon season change. SO<sub>4</sub><sup>2-</sup> concentration shows a significant decrease (p-value, 0.039) in winter to summer season change and increases significantly (p-value, 0.011) in summer to post-monsoon season. Among all 18 parameters, only Ca, Mg, K, HCO<sub>3</sub><sup>-</sup> and DO show significant changes in mean behaviour post-monsoon to last winter season change. All other parameters do not show any significant seasonal change over a period of a year. Among all the parameters, five parameters show significant changes in mean behaviour, hence the overall natural behaviour of water quality parameters gets changed in each season.

**Cluster Analysis:** Since the overall general behaviour of water parameter changes in each season, cluster analysis is applied to water quality data sets of three seasons to classify the sampling sites and to study the spatial variability of water

quality and dendrograms with linkage distance as  $D_{link}/D_{max}$ , multiplied by 100 to standardize was generated. For the winter season (Fig. 2) with linkage distance as  $D_{link}/D_{max}$ < 60, three statistically significant clusters are formed. Cluster-I consists of S1, S3, S4, S5, S6, S7, S9 and S15 sites. Cluster –II consists of S2, S8, S11 and S14 sites whereas cluster-III consists of S10, S12 and S13. For the summer season (Fig. 3) with linkage distance as  $D_{link}/D_{max}$ < 100, three statistically significant clusters are formed. Cluster-I consists of S5, S7, S9, S13 and S14 sites. Cluster –II consists of S1, S2, S4, S6, S10 and S11 sites whereas cluster-III consists of S3, S8, S12 and S15.

For post-monsoon season (Fig. 4) with linkage distance as  $D_{link}/D_{max}$ < 60, three statistically significant clusters are formed. Cluster-I consists of S7, S8, S10, S11 and S12 sites. Cluster –II consists of S3, S9, S13 and S15 whereas cluster-III consists of S1, S2, S4, S5, S6 and S14. The clusters generated have similar characteristic features. It implies that for rapid water quality assessment, only one site from each cluster may determine all water properties. This information is useful for further sampling. Similarly, CA was performed to identify the relationships among the trace metals and their possible sources and a dendrogram was generated (Fig. 5).

All the eight trace metals are grouped into two statistically significant clusters with high linkage distance  $D_{link}/D_{max}x100 < 60$ . Cluster-I consists of Fe and Ba whereas cluster-II consists of Zn, Cu, Ni, As, Mn and Pb. Cluster-I has a high mean concentration compared to cluster-II trace metals.

Parameters	Winter to Summer	Summer to Post-	Post-monsoon to Winter
nH	0.215	0 534	0.439
FC	0.215	0.000	0.134
EC	0.031	0.090	0.134
TDS	0.100	0.155	0.540
Ca	0.093	0.762	0.021
Mg	0.043	0.671	0.006
Na	0.842	0.282	0.532
K	0.009	0.420	0.003
HCO <sub>3</sub> -	0.088	0.859	0.000
Cl-	0.000	0.000	0.222
NO <sub>3</sub> -	0.081	0.209	0.575
SO4 <sup>2-</sup>	0.039	0.011	0.136
Hardness	0.030	0.033	0.671
DO	0.179	0.000	0.000
BOD	0.043	0.854	0.111
COD	0.035	0.564	0.171
Turbidity	0.081	0.035	0.756
SAR	0.207	0.463	0.741
MPN	0.454	0.364	0.879

Table 4Two Sample Paired t-test analysis: P- value Table of Water Data

Note: Bold value represents significant p-values



Figure 2: Cluster Tree for winter season



Figure 3: Cluster Tree for summer season



Figure 4: Cluster Tree for post-monsoon season



**Figure 5: Cluster Tree for Trace metals** 

	Table 5				
Factor Analysis-	Varifactors of water	samples	for	winter	season

Parameters	1	2	3	4	5	6	7
TDS	0.909	-0.035	-0.274	-0.007	0.054	-0.182	0.026
Hardness	0.753	-0.149	-0.310	0.247	0.026	-0.104	0.047
EC	-0.672	0.314	-0.227	-0.273	0.275	0.211	0.232
MPN	0.587	-0.511	-0.102	0.151	0.521	0.134	0.138
Turbidity	-0.573	0.156	0.198	0.544	0.440	0.002	-0.049
Na <sup>+</sup>	0.565	0.390	-0.020	-0.294	0.094	-0.153	0.041
pН	-0.543	-0.087	0.234	0.401	-0.053	-0.257	-0.417
BOD	0.308	0.761	0.509	0.086	-0.035	0.138	0.074
COD	0.308	0.761	0.509	0.086	-0.035	0.138	0.074
<b>SO</b> <sub>4</sub> <sup>2-</sup>	0.300	-0.553	0.247	-0.697	0.008	-0.001	-0.124
SAR	0.106	-0.213	0.850	-0.158	0.297	-0.180	0.175
DO	0.366	-0.002	0.679	0.115	-0.530	0.004	0.023
$\mathbf{K}^+$	0.169	0.454	0.046	-0.678	0.445	0.032	-0.119
Cl	0.481	0.244	-0.332	0.592	0.096	0.074	0.386
$Mg^{2+}$	0.347	0.125	0.058	0.221	0.593	0.286	-0.582
Ca <sup>2+</sup>	0.076	0.178	-0.408	-0.165	-0.417	0.692	-0.211
NO <sub>3</sub> -	0.411	0.456	-0.326	0.027	-0.191	-0.486	-0.415
HCO <sub>3</sub> -	-0.484	0.500	-0.441	-0.266	0.113	-0.403	0.153
Eigen Values	4.348	2.849	2.674	2.199	1.710	1.231	1.064
Variance( $\sigma^2$ )%	24.143	15.825	14.854	12.217	9.498	6.837	5.854
Cumulative $\sigma^2$ %	24.143	39.968	54.822	67.039	76.537	83.374	89.228

Note: Bold value represents strong and moderate loading

**Principal component analysis/Factor Analysis:** PCA/FA was performed on the normalized data to compare the compositional structure between analyzed water samples and to identify the factors which influence each of them. PCA applied to winter data and post-monsoon data yields seven PC's each whereas yields six PCs for summer data with Eigen values >1. An Eigen value is the measure of the significance of the factor and the values of more than 1 are considered as significant<sup>1</sup>. FA was performed on PCs results in varifactors (VF). Projections of the original variables on the subspace of the principal components are loadings and coincide with the correlation coefficients between variables

and principal components. Loading factors of VF are considered as 'strong', 'moderate' and 'weak' depending on absolute loading values >0.75, 0.75-0.50 and 0.50-0.30 respectively. VFs so formed explain 89.23%, 79.20% and 89.88% of the total variation for winter, summer and postmonsoon seasons respectively.

For winter data (Table 5), VF1 explains 24.14% of the total variance and has strong positive loading on TDS and hardness, has moderate positive loading on MPN and sodium and moderate negative loading on EC, turbidity and pH.

Parameters	1	2	3	4	5	6				
Hardness	0.859	0.293	0.018	0.208	0.147	0.096				
TDS	0.849	0.211	0.056	0.327	0.163	0.101				
COD	-0.662	0.085	0.671	0.025	0.191	0.028				
BOD	-0.649	0.103	0.688	0.035	0.167	0.018				
HCO3 <sup>-</sup>	-0.557	0.172	-0.502	0.277	0.189	0.386				
Cl	0.138	0.933	0.131	-0.040	0.087	-0.093				
NO <sub>3</sub> -	0.055	0.736	-0.004	0.198	-0.431	0.087				
SO4 <sup>2-</sup>	0.207	-0.681	0.416	0.209	0.157	0.312				
EC	0.155	0.627	0.189	0.173	0.523	-0.133				
Na <sup>+</sup>	-0.038	-0.525	0.073	0.784	0.090	-0.221				
K <sup>+</sup>	0.219	0.108	0.722	-0.180	-0.432	0.181				
SAR	-0.275	0.190	0.233	0.621	0.315	-0.062				
DO	0.193	0.002	-0.086	0.523	-0.228	0.530				
PH	0.337	-0.157	0.195	0.439	-0.582	-0.422				
MPN	0.465	-0.251	0.063	-0.245	0.353	0.568				
$Ca^{2+}$	-0.377	0.135	0.218	0.068	-0.415	0.482				
$Mg^{2+}$	-0.496	0.249	-0.362	0.233	-0.163	0.316				
Turbidity	0.458	0.034	0.323	-0.201	-0.007	0.199				
Eigen Values	3.807	2.941	2.318	2.002	1.647	1.54				
Variance $(\sigma^2)$ %	21.151	16.341	12.877	11.122	9.149	8.555				
Cumulative $\sigma^2$ %	21.151	37.492	50.369	61.491	70.64	79.195				

 Table 6

 Factor analysis- Varifactors of water samples for summer season dataset

Note: Bold value represents strong and moderate loading

 Table 7

 Factor Analysis- Varifactors of water samples for Post-monsoon dataset

Parameters	1	2	3	4	5	6	7
TDS	0.870	-0.016	0.093	0.230	-0.105	-0.316	0.048
Hardness	0.853	0.105	0.108	0.236	-0.092	-0.335	-0.138
HCO <sub>3</sub> -	-0.660	-0.178	-0.140	0.239	-0.287	-0.118	0.514
SAR	0.654	-0.411	-0.043	-0.087	-0.037	0.501	-0.076
$Mg^{2+}$	0.634	0.326	-0.346	-0.311	-0.219	-0.187	0.107
Na <sup>+</sup>	0.572	-0.660	0.302	-0.069	0.019	0.262	0.007
$SO_4^{2-}$	0.539	-0.245	0.124	0.441	0.439	-0.357	0.124
COD	0.266	0.860	-0.060	-0.097	0.009	0.373	0.041
BOD	0.309	0.826	-0.108	-0.122	0.006	0.369	0.053
NO <sub>3</sub> -	0.117	0.568	-0.553	0.130	0.416	-0.271	0.124
K <sup>+</sup>	0.022	-0.559	-0.672	0.060	0.220	0.241	-0.034
MPN	-0.278	0.316	0.811	0.092	-0.073	0.093	0.270
Ca <sup>2+</sup>	-0.290	0.060	-0.765	0.273	0.002	0.083	-0.41
PH	-0.458	0.134	0.081	0.768	0.327	0.172	-0.014
EC	0.213	0.055	0.441	0.570	-0.076	0.334	-0.313
Cl-	-0.200	0.324	0.040	0.295	-0.619	-0.258	-0.436
DO	0.126	-0.380	-0.463	0.274	-0.595	0.096	0.248
Turbidity	-0.443	-0.246	0.261	-0.495	0.145	-0.282	-0.413
Eigen Values	4.215	3.305	2.769	1.919	1.442	1.426	1.101
Variance $(\sigma^2)$ %	23.415	18.363	15.381	10.664	8.012	7.925	6.116
Cumulative $\sigma^2$ %	23.415	41.778	57.159	67.823	75.835	83.76	89.876

Note: Bold value represents strong and moderate loading

VF2 explains 15.83% of the total variance and has strong positive loading on BOD and COD, moderate positive loading on  $HCO_3^-$  and moderate negative loading on  $SO_4^{2-}$ . VF3 explains 14.85% of the total variance and has strong positive loading on SAR and moderate positive loading on BOD, COD and DO. The remaining four VFs explain 34.41% of the total variance. For summer data (Table 6). VF1 explains 21.15% of the total variance and has strong positive loading on hardness and TDS and moderate negative loading on BOD/COD and HCO3<sup>2-</sup>. VF2 explains 16.34% of the total variance and have strong positive loading on chloride, moderate positive loading on EC and NO<sub>3</sub><sup>-</sup> and moderate negative loading on sodium and SO42-. VF3 explains 12.88% of total variance and has moderate positive loading on BOD, COD and potassium (K) and moderate negative loading on HCO<sub>3</sub><sup>-</sup>.

The remaining three VFs explain 28.83% of the total variance. For post-monsoon season (Table 7), VF1 explains 23.42% of the total variance and has strong positive loading with TDS and hardness, moderate positive loading with SAR, magnesium, sodium and sulphate and moderate negative loading with  $HCO_3^-$ . VF2 explains 18.36% of the total variance and has strong positive loading with BOD and COD, moderate positive loading with  $NO_3^-$  and moderate negative loading with  $K^+$ .

VF3 explains 15.38% of the total variance and has strong positive loading with MPN and strong negative loading with  $Ca^{2+}$  and has moderate negative loading with  $NO_3^-$  and  $K^+$ . The remaining four VFs explain 32.72% of the total variance.

Positive loading on  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  and hardness can interpret the mineral composition of water. This clustering of variables points to a common origin for these minerals. The positive loading on TDS, DO, BOD, COD represents high levels of dissolved organic matter consuming the large amounts of oxygen<sup>20</sup>. For trace metals (Table 8), three VFs are generated with Eigen value >1, which explains 72.89% of the total variance. VF1 explains 38.79% of the total variance and has strong positive loading on zinc (Zn), copper (Cu) and nickel (Ni) and has moderate positive loading on iron (Fe) and barium (Ba).

VF1 points towards the common sources of minerals. VF2 explaining 20.41% of the total variance and has strong negative loading on Manganese (Mn) and moderate positive loading on Arsenic (As). VF3 explains 13.66% of the total variance and has moderate negative loading on arsenic (As) and positive loading on lead (Pb).

Trace Metals	1	2	3
Zn	0.843	0.343	0.192
Cu	0.802	-0.132	0.259
Ni	0.752	-0.331	0.274
Fe	0.651	-0.340	-0.374
Ba	0.636	0.010	0.204
Mn	-0.174	-0.896	-0.121
As	0.348	0.650	-0.507
Pb	-0.452	0.223	0.678
Eigen Values	3.103	1.634	1.093
Variance ( $\sigma^2$ )%	38.79	20.428	13.659
Cumulative $\sigma^2$ %	38.79	59.218	72.877

 Table 8

 Factor Analysis- Varifactors for Trace metal analysis of water samples

Note: Bold value represents strong and moderate loading

Location	Winter	Summer	Post- monsoon	Location	Winter	Summer	Post- monsoon			
S1	24.2	24.0	23.0	S9	24.0	25.4	25.1			
S2	28.0	24.6	23.6	S10	25.8	24.6	26.7			
S3	25.4	29.8	23.0	S11	24.5	25.4	27.3			
S4	27.2	26.3	25.0	S12	27.9	30.6	27.1			
S5	25.8	22.1	25.6	S13	26.1	24.0	25.0			
<b>S</b> 6	24.8	26.1	26.0	S14	24.6	23.8	25.2			
<b>S</b> 7	24.3	24.5	26.6	S15	23.4	26.9	25.8			
S8	25.6	26.4	26.9							

Table 9 Water Quality Index for each season



Figure 6: Piper diagram for winter season



Figure 7: Piper diagram for summer season



Figure 8: Piper diagram for post-monsoon season

**Water Quality Index:** The water quality index of all the sites is calculated and is summarised in table 8. All the water quality indices in all seasons are between 22% to 31% showing that the water is of excellent quality and best for drinking purposes. As the expected maximum value of the water quality index is found in the summer season as 30.6%. The aggregate water quality index for the study region is 25.5%

**Piper Diagram:** In the piper diagram, the milliequivalent percentage of the major cations and anions are plotted in a separate triangle. These plotted points in triangular fields are further projected into the central diamond field. This diamond field provides the overall character of the water. Piper diagrams were plotted for the winter season (Fig. 6), summer seasons (Fig. 7) and post-monsoon season (Fig. 8). In each piper diagram, all projected points in diamond fields are in the right quadrant and show water type is sodium chloride water like marine and deep ancient groundwater.

#### Conclusion

In this study, different multivariate statistical tools were used to evaluate spatial variation in water quality around JNPP. Hierarchical cluster analysis helps to group the fifteen sampling sites into three clusters of similar characteristics. Extracted grouping information can be used for reducing the sampling sites without losing much information. PCA/FA results considerable data reduction, since out of all parameters show only TDS, Hardness, BOD, COD, SAR explains 89% of data variability for the winter season, TDS, hardness, Cl<sup>-</sup> and Na explain 79% of data variability for summer season and TDS, Hardness, BOD, COD, Ca, pH and MPN explain 90% of data variability for post-monsoon season. Piper diagram indicates that the primary salinity ("non-carbonate alkali") exceeds 50% i.e. chemical properties of water are dominated by alkalies and strong acids.

Trace metal analysis indicates that all trace metals are within the normal range. Cd, Cr and Co are below detection level along with 'As' for 4 sampling sites. Among all 18 parameters, only Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and DO show significant changes in mean behaviour over post-monsoon to last winter season change. All water quality indices of the study region indicate that water is excellent, not contaminated and fit for drinking purposes. Thus, the multivariate statistical techniques along with water quality indices and piper diagram can be used to analyze and interpret the complex dataset on water quality and understanding their variations.

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