



Contrasting distribution of arsenic and uranium in the groundwater of alluvial plains, North India: Implications for origin, fate control, and Health Perspectives

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Submission Date : 10-Aug-2023

PROPOSAL DETAILS

(PDF/2023/002841)

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Dr. Ritu Bala ritubala95@gmail.com (Department of Civil Engineering) Contact No : +919501710328 Date of Birth : 22-Apr-1995 Name of Father/Spouse : Prehlad Kumar	Indumathi M Nambi indunambi@iitm.ac.in Professor(Department of Civil Engineering) Indian Institute of Technology Madras I.i.t. post office chennai, Chennai, Tamil nadu-600036 Contact No. : +919444687042 Registrar Email : registrar@iitm.ac.in No. of PHD Scholars : 3 No. Post-Doctoral Fellow : 1

Details of Post Doctorate

Ph.D. (Hydrology) [Degree Awarded on : 06-Dec-2022]

INVESTIGATIONS OF POTENTIAL SOURCE, MOBILIZATION AND HEALTH RISK ASSESSMENT OF ELEVATED GROUNDWATER URANIUM IN THE CENTRAL PART OF MALWA REGION, PUNJAB, INDIA

Research Supervisor/Guide & Institution :

Dr. Debabrata Das

Panjab University, Chandigarh

Brief details of Thesis work :

In the doctoral research, detailed micro level investigations have been carried out on the hydrogeological, hydrolithological, hydrochemical and geochemical framework with the underlying purpose of providing complete picture of uranium contamination in aquifers of the region. Groundwater is used for domestic and irrigation purposes in the study area, which has resulted in overexploitation of groundwater resources. Thus, groundwater quality is a matter of high concern in the region from past few decades especially after the identification of high uranium levels in groundwater. An attempt has been made in the present work to fill the missing gap of detailed sediment study in the region that is required for the source identification of groundwater uranium.

Uranium concentration in groundwater of the region is seen to vary from 4.26 to 318.03 µg/l with an average of 59 µg/l. Spatial distribution maps and the vertical graphs of ions shows that the concentration of ions is higher in the southern part and shallow aquifers of the region. Climate plays an important role in the increasing concentration towards southern portion. Rainfall decreases in the southwest direction and aridity increases resulting in higher evaporation. This leads to the high conductivity and higher ion concentration in the south. Higher concentration observed at shallow depth may have resulted due to the soil mineralization with rapid recharge of water through shallow aquifers along with anthropogenic input whereas source of major ions in the deeper aquifers is considered to be lithogenic, resulting from dissolution of rocks and minerals of aquifer sediments.

Groundwater decline has been observed in most of the parts of region as seen from the long term decadal fluctuation of water table. Water level decline results in increased exposure to the contaminants due to change in redox environment. Aquifers show mixed redox environment with oxic conditions being more prevalent in shallow aquifer and hence results in uranium solubility.

Bicarbonate and EC concentration is found to be higher in the groundwater and correlates well with the high uranium concentration. These are identified as the controlling factors of uranium mobilization in both the aquifers. However, correlation of sulphate and chloride is seen only in the shallow aquifer and gives indication towards anthropogenic enrichment. Strong correlation of uranium with electrical conductivity and alkalinity imply that weathering of carbonates and desorption of uranium from mineral surface is major cause of uranium mobilization in the aquifer system. Thus, redox chemistry and carbonate alkalinity are recognised as primary factors controlling U mobility.

Environmental stable isotopes shows the evaporation signature in both the aquifers indicating the contribution of irrigation or evaporated water to the aquifer system and shows that irrigation return flow count as major factor for groundwater recharge thus might have resulted in higher concentration of U in the groundwater.

Geochemical analysis shows the mean uranium concentration of 42.55, 49.12 and 34.60 Bq/kg in the top (0-300 cm), middle (300-600 cm) and bottom (600-900 cm) aquifer sediments respectively of agricultural regions. Mean levels are 33.12, 46.66 and 35.86 Bq/kg respectively in the undisturbed regions. Levels are higher in the agricultural than the undisturbed regions and the probable cause of this difference is the use of high amount of fertilisers as levels are comparable after depth interval of 600 cm at both the lands. However, the value is higher than the global average even in the undisturbed areas and indicates the geogenic presence of radionuclides in the study region with anthropogenic enrichment.

Soil texture also controls the uranium levels. Higher concentration is seen in clay sediments at top than the sandy sediments at bottom. Vertical movement of uranium can be traced from the sub-surface sediments through weathering or leaching due to the prevailing oxidising conditions.

Mobilization of uranium from the sediment gives a hint that soil of the region acts as the source and sink for uranium with changing redox conditions and counts to be the major factor for the high uranium detected in groundwater of the region.

Source identification of U is a complex process especially in locations with anthropogenic input. There exist regional and local differences including aquifer differences and natural heterogeneity. Lithology and alluvium composition imply that the uranium is concentrated in discrete layers in alluvial sediments and comprises of material eroded from ore-rich strata in the north (tertiary Siwalik sediments). Uranium has been cycling in alluvial sediments (solid phase) and groundwater (dissolved phase) as a result of rapid changes in redox chemistry. Specifically, these activities take place at the interface of high and low permeability sediments, where groundwater flowing in coarse-grained material of high permeability interacts with less permeable domains by diffusion into and out of the silt and clay sediments.

Along with the natural background of high U mobility, agricultural activities trigger the mobility of U with the infiltration of irrigational recharge and increase of bicarbonate content in the groundwater.

Direct anthropogenic U input cannot be assured however, anthropogenic inputs from fertilizers and irrigation water recharge plays vital role in the increased uranium concentration of shallow aquifer and cannot be ignored.

Transfer of uranium from the soil-water system to the food chain is seen in the current study. Very high uranium content is observed in the Barseem leaves used for cow feeding and the content varies in different parts of same plant. Hazard index value also shows risk to the population exposed and poses significant cancer risk due to the carcinogenic properties of uranium.

Technical Details :

Research Area : Earth & Atmospheric Sciences (Earth & Atmospheric Sciences)

Project Summary :

The proposed project will study the environmental occurrence and fate of the elements Uranium (U) and Arsenic (As) in groundwater and sediments of alluvial plains of north-west India (state of Punjab).

As and U increasingly finds themselves in the spotlight of scientific attention due to potential public health impacts, especially when populations are exposed to elevated concentrations in drinking water.

U and As mobilization from natural (geogenic) sources- and thus their input into groundwater and ultimately drinking water- is governed by prevailing hydrogeochemical conditions and man-made influences. Investigating this complex interplay is indispensable for understanding distribution and dynamics in environmental systems, which in turn is the basis for their sustainable use, including protection of their users. In the proposed region, widespread elevated U and As concentrations in groundwater used for drinking water supply are known for about a decade. However, investigations so far were largely limited to the groundwater itself and in case of U, sources, sinks, and responsible accumulation and mobilization processes are still unknown. This gap will be addressed in the proposed project by characterizing aquifer sediments and groundwater from boreholes using a variety of field and laboratory methods, complemented by hydrogeochemical modelling. We also propose to correlate the drinking water data with the diseases prevalent in the region (cancer belt), so as to have a database of correlating these contaminants to the health factors globally. If successful, the developed toolbox and identified processes may be transferable to similarly affected regions worldwide, and significantly contribute to the characterization of geogenic and anthropogenically influenced trace element fluxes in subsurface environments. The project findings will also be used to inform and sensitize scientific and political decision-makers, and the exposed population in Punjab.

Objectives :

• To Understand the spatial and vertical distribution pattern of contaminants in the aquifer system of region.

• The sources and sinks of contaminants and the responsible mobilisation and accumulation processes will be identified and characterised using an ambitious multi-method and multidisciplinary approach.

• Determine the spatial relationship between the incidence rates of bladder, liver, lung, breast, and kidney cancers and the contaminant concentrations.

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Keywords :

Arsenic, Uranium, Alluvial Plains, Groundwater, Hydrochemistry, Public health

Expected Output and Outcome of the proposal :

Current study is indispensable for understanding the distribution and dynamics of these contaminants in the environmental system, which is the basis for their sustainable use, including the protection of their users. Contrasting behaviour of elements such as As and U has implications for the risk management and remediation measures. The common strategies of mitigation should be adopted in areas with high concentration. Measures intended to address one may end up being hazardous for the other. The results will contribute to the health diseases of the people residing in the region. In addition, the project findings will also reduce the health expenses of the people residing in the region. In addition, the exposed population.

Reference Details :

S.No	Reference Details
1	Dr. Debabrata Das, Assistant Professor, Panjab University, Chandigarh [+91986651879] debabradas@pu.ac.in
2	Prof. Elango Lakshmanan, Visiting Faculty, Hydraulics and Water Resource Engineering, IIT Madras, Chennai, Tamil Nadu [+919444118629] elango@iitm.ac.in

Detailed Methodology and Work Plan:

The toolbox required to address the formulated objectives and associated research questions has to account for the proposed study being located where different environmental compartments (water, rock and soil) intersect. To accomplish this, combinations of multiscale field methods and laboratory experiments are required, supported by suitable modelling tools. The most decisive point in doing so is the inclusion of both the solid and the fluid phases, participating in water-rock interaction in the aquifer. If looking at the environmental behaviour of elements of concern, like in this case U and As, it is insufficient to only take bulk contents in sediments or rocks into account- we have to consider the potentially mobile fraction which is mostly considerably lower than the total content. This can be accomplished by mobility experiments like sequential extraction procedures and circular column tests which mean relatively high time commitments but may generate a multitude of valuable information as we can also conclude from the element's solid fractionation to hydrogeochemical processes possibly remobilizing it. These conclusions, in turn, can then be tested in further batch or column experiments. Once confident that a possible release (or accumulation) mechanism was identified, hydrogeochemical modelling can be a very powerful tool to reproduce and further comprehend these processes in a given environment as it is able to take physico-chemical conditions, hydrochemical, geochemical and mineralogical data into account, and allows for simulation, extrapolation and forecast of hydrogeochemical evolution of the aquifer. This way, the approach also becomes multiscale – from studying the distribution and geochemical association on the μm scale in thin sections, via conditions governing the vertical distribution in sediments and hydrochemical conditions in the aquifer as quantified in sediment and groundwater samples from boreholes (m to hundreds of m scale), to the status and evolution of the whole aquifer system as concluded from widely distributed spatial data and extrapolation of conditions and hydrogeochemical evolution (km to hundreds of km scale) interpolated in geostatistical exercises and simulated using numerical hydrogeochemical modelling. Individually, the mentioned methods have been applied before to tackle similar research questions, but their comprehensive combination is not found in earlier studies. The key method novelty here is linking this variety of multiscale and multidisciplinary techniques. Suchlike multimethod approaches are by their nature site-specific and thus local and regional peculiarities must be taken into account. Therefore, they most probably must be readjusted along the way, possibly several times, as successively more data is collected, and more knowledge is gained: the ideal method combination for the given proposed project will yet have to be established. For instance, if we find high bulk U contents (geochemical analysis) in a sediment layer partly composed of carbonates (mineralogical analysis) in reaction contact with high-U groundwater (hydrochemical analysis), we will have to adjust further experiments according to that we e.g., implement an extraction step targeting carbonates in the design of the sequential extraction procedure (U mobility analysis), adjust sample selection in mineral targets for LA-ICP-MS (U distribution on a microscale), or consider the respective carbonate phases in (inverse) reaction

simulations and forecast of hydrochemical evolution (hydrogeochemical modelling). Also, the health data set would be collected from the local population during field surveys, Indian Council of Medical Research and National Family Health Surveys, Postgraduate Institute of Medical Education & Research and other competent authorities. In any case, I am convinced that in this context, the whole is much more than the sum of its parts, and the efforts of applying all these methods (instead of only a small selection from the toolbox as we are seeing in the current literature) will pay off by generating the extra information required to address the ambitious objectives of the proposed project, and act as a toolbox template for future studies in similarly affected regions worldwide.

Work Methodology in Brief:

The data collected in a rather unconventional combination of field and laboratory methods will then be evaluated regarding the research questions using hydrochemical, different statistical, geostatistical, geochemical, and hydrogeochemical modelling approaches.

Field based:

- Large number of representative groundwater samples would be collected from the whole region covering both the shallow and deeper aquifers.
- Sediment samples would be collected by borehole drilling from sites of high concentration observed.
- Foodgrain samples would be collected from all the locations.
- Health data set would be collected from the Local population during field surveys, Indian Council of Medical Research and National Family Health Surveys, Postgraduate Institute of Medical Education & Research and other such bodies.

Laboratory based:

- Hydrochemical analysis would be carried out in the groundwater samples using ICP-MS.
- Bulk geochemical analysis using ICP-MS followed by HF-HCl-HNO₃ digestion.
- Mineralogical analysis will be carried out by using SEM-EDS and XRD technique.
- To characterise the solid phase fractionation and the remobilisation potential of U & As in the sediments, a sequential extraction procedure will be carried out for selected samples (sample selection following geochemical and mineralogical characteristics including high content observed).
- Circular column experiments with representative sediment cores and groundwater will provide information on the long-term mobility behaviour.
- For the hydrogeochemical modelling of subsurface conditions, mineral saturation states, hydrochemical speciation and water-mineral interaction processes, the freely available software PhreeqC (Parkhurst and Appelo 2013) will be used.

Work plan:

After the in-depth literature review and collection of available datasets, a first field campaign will be carried out after the project beginning in which water samples would be collected from the whole area on the basis of micro watershed divisions. Aqueous sample analysis would be carried out for the major and trace element measurement in the laboratory. After obtaining the results, drilling locations would be decided for the sediment collection on the basis of higher concentration observed in aqueous samples. Data would be processed for publication.

In the second phase, sediment samples would be collected metre by metre by the borehole drilling from four boreholes. Here, the protection of the samples from oxidation by using an inert gas (argon or nitrogen) should be emphasised. The boreholes will then be developed to groundwater monitoring wells, which will be regularly sampled and hydrochemically analysed at different depths. Most suitable sites for drilling boreholes and sampling sediments will be in the hydrogeochemical contact with the U-rich groundwater and As-rich groundwater. In these zones, the probability to identify processes responsible is considered highest. The sediment collected would be transferred to the laboratory. After the bulk geochemical analysis, sequential extraction procedures and circular column experiments would be carried out to characterise the solid phase fractionation and remobilisation potential of both the elements. In the later phase PhreeqC would be utilised for the hydrogeochemical modelling of subsurface conditions, mineral saturation states, hydrochemical speciation and water-mineral interaction processes. Successful completion of field work and the subsequent multimethod laboratory approach eventually resulting in the manuscript submission to international peer-reviewed journals will be the key intermediate goals.

Also, in the third phase, during visit to field, food grain samples would be collected. In the final phase, the results produced would be utilised to inform the scientific and political decision-making authorities to resolve the problem and follow up activities will be considered in further research.

PROFORMA FOR BIO-DATA (to be uploaded)

1. Name and full correspondence address: Dr. Ritu Bala, #3531, Sector 37D, Chandigarh-160036
2. Email(s) and contact number(s): ritubala95@gmail.com and 9501710328
3. Institution: Panjab University, Chandigarh
4. Date of Birth: 22-04-1995
5. Gender (M/F/T): F
6. Category Gen/SC/ST/OBC: General
7. Whether differently abled (Yes/No): No
8. Academic Qualification (Undergraduate Onwards)

	Degree	Year	Subject	University/Institution	% of marks
1.	Graduation	2012-2015	Geology (HS)	Panjab University, Chandigarh	73
2.	Post-graduation	2015-2017	Geology (HS)	Panjab University, Chandigarh	83
3.	Ph.D.	2018-2022	Hydrogeology	Panjab University, Chandigarh	
9. Ph.D thesis title, Guide's Name, Institute/Organization/University, Year of Award.
Investigations of Potential Source, Mobilization and Health Risk Assessment of Elevated Groundwater Uranium in the Central Part of Malwa Region, Punjab, India; Dr. Debabrata Das; Panjab University, Chandigarh; 2022
10. Work experience (in chronological order): NA

11. Professional Recognition/ Award/ Prize/ Certificate, Fellowship received by the applicant.

S.No.	Name of Award	Awarding Agency	Year
1.	Gold Medal	Panjab University, Chandigarh	2017
2.	DST-INSPIRE Fellowship	Government of India	2018
3.	Fellowship for attending Summer School at Germany	DAAD	2018
4.	Young Scientist award	National conference held at CMPDIL, Ranchi	2019

12. Publications (*List of papers published in SCI Journals, in year wise descending order*).

S.No.	Author(s)	Title	Name of Journal	Volume	Page	Year
1.	Ritu Bala, Karanveer, Debabrata Das	Occurrence and behaviour of uranium in the groundwater and potential health risk associated in semi-arid	Groundwater for Sustainable Development	17	10031	2022

		region of Punjab, India.				
2.	Ritu Bala, Debabrata Das, Karanveer, Nabanita Naskar, Susanta Lahiri	Vertical distribution and radiological risk assessment of natural radionuclides in the alluvial soil profile of south-west Punjab, India.	Journal of Radioanalytical and Nuclear Chemistry	331	2561-2572	2022
3.	Karanveer, Ritu Bala, Debabrata Das	Geochemical and health risk assessment of potentially toxic trace elements and nitrate via groundwater in agro-ecosystem of alluvial plain Punjab, India	Human and Ecological Risk Assessment: An International Journal	28	983-1011	2022

13. Detail of patents: NA

14. Books/Reports/Chapters/General articles etc.

S.No.	Title	Author's Name	Publisher	Year of Publication
1.	Geogenic uranium mobilization in the alluvial aquifers of north-west India and extent of contamination- a review	Ritu Bala, Debabrata Das, Karanveer, Prakash Tiwari, Shivam Sharma, Ramkrishan Mondal	Publication in Conference Proceedings- HYDRO 2022	Accepted

15. Any other Information (maximum 500 words)

I have attended International German School of Hydrology on Groundwater and mining at Ruhr University of Bochum, Germany as Fully sponsored participant. Also, awarded with International Travel grant from SERB for Goldschmidt 2022, held at Hawaii. It wasn't availed due to unavailability of USA visa appointments.

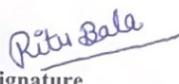
I have expertise in the Field sample collection, chemical analysis, various softwares (such as Phreqqc, Grapher, Aquachem, Rockworks and ArcGIS) along with the equipment handling such as AAS, ICP-MS and Microwave Digestor.

Undertaking by the Fellow

I, Dr. Ritu Bala, Daughter of Shri Prehlad Kumar, resident of Mansa, Punjab agree to undertake the following, If I am offered the SERBN-PDF

1. I shall abide by the rules and regulations of SERB during the entire tenure of the fellowship.
2. I shall also abide by the rules, discipline of the institution where I will be implementing my fellowship
3. I shall devote full time to research work during the tenure of the fellowship
4. I shall prepare the progress report at the end of each year and communicate the same to SERB through the mentor
5. I shall send two copies of the consolidated progress report at the end of the fellowship period.
6. I further state that I shall have no claim whatsoever for regular/permanent absorption on expiry of the fellowship.

Date: 09/08/2023


Signature



Roll No. 5876

**INVESTIGATIONS OF POTENTIAL SOURCE, MOBILIZATION AND HEALTH RISK ASSESSMENT
OF ELLEVATED GROUNDWATER URANIUM IN THE CENTRAL PART OF MALWA REGION,
PUNJAB, INDIA**

Ph.D thesis submitted by Ritu Bala
In the Faculty of Science/Geology
Panjab University, Chandigarh

Citation

Uranium (U) occurrence in groundwater of southwest Punjab is investigated using hydrochemical and geochemical methods due to its alarming levels, poor understanding of source, and mobility. U content is found to be higher in 76% of samples with shallow aquifers being more contaminated. Palaeochannel-controlled geogenic U mobilization is seen from northeast Siwalik sediments. Thus, alluvial soil acts as a source and sink of U with agricultural activities triggering its mobilization. U has been cycling in alluvial sediments and groundwater as a result of rapid changes in redox chemistry, mostly from lower permeability sediments. Hazard index value also shows significant carcinogenic risk to the population exposed.

W
Registrar



Panjab University



Doctor of Philosophy

(In the faculty of Science)

Certified that Ritu Bala, Regd. No. 12-gd-22, daughter of Shri. Prehalad Kumar, and of the Punjab State, has obtained the degree of Doctor of Philosophy of this University on the result of the examination held in 2022.

Given under the seal of the University



Controller of Examinations

Yash

Registrar

Vice Chancellor

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Chancellor

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CENTRAL BOARD OF SECONDARY EDUCATION
विषयवार निष्पादन का विवरणSTATEMENT OF SUBJECT WISE PERFORMANCE
माध्यमिक स्कूल परीक्षा, 2010

ALL INDIA

SECONDARY SCHOOL EXAMINATION, 2010

नाम Name

RITU BALA

अनुक्रमांक Roll No. 2186105

माता का नाम Mother's Name

SLOCHANA DEVI

पिता का नाम Father's Name

PREHLAD KUMAR

जन्म तिथि Date of Birth

22ND APRIL

NINETEEN HUNDRED NINTY FIVE

विद्यालय School

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विषय कोड Subject Code	विषय Subject	ग्रेड Grade	ग्रेड बिंदु (जी पी) Grade Point (GP)
101	ENGLISH COMM.	B2	07 (SEVEN)
085	HINDI COURSE-B	A2	09 (NINE)
041	MATHEMATICS	A2	09 (NINE)
086	SCIENCE	B1	08 (EIGHT)
087	SOCIAL SCIENCE	B1	08 (EIGHT)
004	PUNJABI	A2	09 (NINE)

संचयी ग्रेड बिंदु औसत (सी जी पी ए) / Cumulative Grade Point Average (CGPA) : 08.2

परिणाम/Result : ELIGIBLE FOR QUALIFYING CERTIFICATE

AB : विषय में अनुपस्थित Absent in the Subject

++ : मिलान / प्रायोगिक कौशल / प्रायोगिक / आंतरिक मूल्यांकन में अनुपस्थित
Absent in Theory / Practical Skill / Practical / Internal Assessment

दिल्ली Delhi

दिनांक Dated

28-05-2010

टिप्पणी / Note:- सोनीपोरा अध्ययन की योजना के अनुसार अतिरिक्त छठे विषय को छोड़कर सभी विषयों में अर्जित ग्रेड बिंदुओं का औसत है।

The CGPA is the average of Grade Points obtained in all the subjects excluding additional 6th subject as per Scheme of Studies.

ग्रेड बिंदु की निरैक्षण्यक समानता तथा अंकों की प्रतिशतता को निम्नानुसार निर्धारित किया जा सकता है :

An indicative equivalence of Grade Point and Percentage of Marks can be assessed as follows :

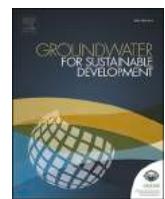
> विषयवार अंकों की निरैक्षण्यक प्रतिशतता = 9.5 x विषय का जीपी Subject wise indicative percentage of marks = 9.5 x GP of the subject.

> अंकों की समग्र निरैक्षण्यक प्रतिशतता = 9.5 x सीजीपीए Overall indicative percentage of marks = 9.5 x CGPA.

परीक्षा नियंत्रक
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Groundwater for Sustainable Development

journal homepage: www.elsevier.com/locate/gsd

Research paper

Occurrence and behaviour of uranium in the groundwater and potential health risk associated in semi-arid region of Punjab, India

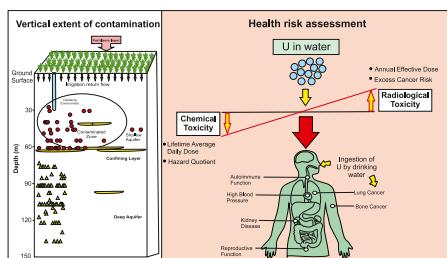
Ritu Bala, Karanveer, Debabrata Das *

Department of Geology, Panjab University, Chandigarh, 160014, India

HIGHLIGHTS

- Shallow alluvial aquifer is more contaminated with high spatial variability.
- U levels are higher along the groundwater flow direction in the SW direction.
- EC, Na^+ , K^+ and HCO_3^- ions are primarily governing the behaviour of uranium.
- Weathering of carbonates is a major cause of uranium mobilization in the aquifers.
- 33% of samples exhibit carcinogenic risk due to U in groundwater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
 Groundwater
 Uranium
 Stable isotope
 Human health risk
 Punjab

ABSTRACT

Occurrence of uranium (U) in the groundwater of south-west Punjab is a matter of great concern due to the rise of contaminant levels at an alarming rate, its spatial and vertical variability and poor understanding of uranium mobility with depth. Present study has been conducted to investigate the vertical extent of contamination and geochemical factors controlling U mobilization in the groundwater of semi-arid Punjab. Out of total 140 samples collected and analyzed, 76% samples have uranium levels greater than the chemical toxicity limit of World Health Organization (WHO, $30 \mu\text{g.L}^{-1}$) and 34% samples have concentration higher than the radiological toxicity limit given by Atomic Energy Regulatory Board (AERB, $60 \mu\text{g.L}^{-1}$). Water at shallow depth ($<60 \text{ m}$) is found to be more contaminated than water at deeper depth ($>60 \text{ m}$) and concentration lies in the range of $4.26\text{--}318.03 \mu\text{g.L}^{-1}$. Spatial distribution graphs are used to identify the hotspots of contamination and concentration is higher in the flow direction of groundwater towards south-west. In both the aquifers, groundwater is alkaline and oxic in character with carbonate weathering as dominant hydrogeochemical process affecting chemical composition of water. Higher uranium concentration is seen in the oxidizing, alkaline and carbonate-rich water. Alkali earth metals (Na^+ & K^+) are also strongly correlated with the uranium in groundwater at both the levels. Use of environmental stable isotopes ($\delta^{18}\text{O}$ & $\delta^2\text{H}$) shows the evaporation signature in both the aquifers. Health risk assessment is carried out and values higher than permissible limit give indication towards the health risk to the population exposed due to the consumption of uranium contaminated water from long time. This study provides

Abbreviations: AERB, Atomic Energy Regulatory Board of India; BDL, Below Detection Limit; Ca^{2+} , Calcium; Cl^- , Chloride; cm, centimeter; EC, Electrical conductivity; HCO_3^- , Bicarbonate; ^2H , Deuterium; K^+ , Potassium; m, meter; mg.L^{-1} , milligram per litre; mg.kg^{-1} , milligram per kilogram; Mg^{2+} , Magnesium; Na^+ , Sodium; NO_3^- , Nitrate; NW, North-west; ^{18}O , Oxygen-18; ORP, Oxidation-reduction potential; PO_4^{3-} , Phosphate; SO_4^{2-} , Sulphate; SW, South-west; TDS, Total Dissolved Solids; U, Total Uranium; WHO, World Health Organization; $\mu\text{g.L}^{-1}$, microgram per litre.

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a strong base for better understanding the source of uranium in the aquifer system of region and the results would be useful for further studies in quaternary alluvial aquifers of semi-arid regions.

1. Introduction

Uranium (U) as a potential drinking water health hazard is brought to the notice after the provisional guideline given by World Health Organization (WHO). Earlier U was not a part of water quality investigations at most of the places and thus the background information on distribution and range of concentration in the groundwater is limited. From past few decades, element concentration in groundwater exceeding the permissible limit of WHO i.e. $30 \mu\text{g.L}^{-1}$ (WHO, 2011a) has become a serious health concern globally. Countries such as Canada (Moss et al., 1983), Finland (Kurtio et al., 2006), New Mexico, USA (Hakonson-Hayes et al., 2002), China (Wu et al., 2014) and Mongolia (Nriagu et al., 2012) have identified uranium in its groundwater. Uranium levels in the groundwater of quaternary fluvial aquifer also exceed the German drinking water limit of $10 \mu\text{g.L}^{-1}$ (Banning et al., 2017).

Uranium is introduced to the groundwater system by the natural geochemical processes (geogenic) or anthropogenic activities (Coyte et al., 2018; Smedley et al., 2006). Geogenic source includes the mineral dissolution of host rocks and sediments along the flow path of groundwater or desorption from the surface of various minerals (Chen et al., 2005; Jerden and Sinha, 2006). In rocks and soil, uranium is present in many major rock-forming minerals and is also incorporated in a number of minor phases. It can also be present on grain boundaries. It is well known that clays, carbonate, Fe, Mn, and Al oxides and hydroxides act as strong adsorbent of uranium (Porcelli and Swarzenski, 2003). Anthropogenic sources of uranium include mining and ore processing of uranium, radioactive material production, and disposal, combustion of fuels, and use of phosphatic fertilizers in agricultural fields (Cothen and Lappenbusch, 1983; Dreeson et al., 1982; Spalding and Sackett, 1972; Tadmor, 1986). However, concentration is highly variable depending on the groundwater chemistry, aquifer characteristics, and bedrock geology (Frengstad et al., 2000).

Redox processes control the enrichment of U in groundwater and its solubility is highly sensitive to the aquifer geochemistry. Fate of the uranium i.e. whether it gets sorbed, mobilized, precipitated or immobilized is decided mainly by its oxidation state and mineral solubility (Maher et al., 2013). Environmental chemistry of uranium is influenced by its oxidation-reduction potential (ORP) because of their redox dependency (Finch and Murakami, 1999). There are three main oxidation states of U(IV, V and VI) in nature, however, U(IV), the reduced form, and U(VI), the oxidized form controls most of the U geochemistry. The solubility of U(VI) is extremely high and oxidizing conditions effectively enhance the uranium movement (Alam and Cheng, 2014). Uranium mobilization is studied by the various complexes formed by it in the water system depending on pH and pCO_2 . At lower pH (<5), dominant species of U is Uranyl ion (UO_2^{2+}), however, UO_2^{2+} forms complexes with carbonate, phosphate, and calcium at higher pHs (Bernhard, 1998; Langmuir, 1978; Porcelli and Swarzenski, 2003).

Uranium concentration is also affected by recharge and discharge from the aquifers and stable isotopes (^{18}O & ^{2}H) are widely used to get an insight to the aquifer recharge system (Kendall and MacDonnell, 1998; Negrel et al., 2003). These environmental tracers are recognized as recorders of important processes like evaporation, transpiration, recycling, and mixing of water (Tarki et al., 2016). Uranium poisoning is a matter of concern more because of its chemical toxicity than its radiological impacts. A considerable body of evidence also suggests that overexposure to uranium causes nephrotoxicity and osteotoxicity (Kurtio et al., 2006). Uranyl ion replaces the calcium in the bone crystal (Moss et al., 1983) and skeleton is the main site of its accumulation (Wrenn et al., 1985).

In India, 16 states have been detected with uranium in its

groundwater. Uranium in groundwater is prevalent in states of Andhra Pradesh (Babu et al., 2008), Karnataka (Brindha and Elango, 2013), Gujarat, West Bengal, Chhattisgarh, Haryana, Himachal Pradesh, Madhya Pradesh, Punjab, and Rajasthan (Coyte et al., 2018). All the states except north-west (NW) India have Pre-Cambrian rocks which are naturally considered to be a source of uranium (Thivya et al., 2016; CGWB, 2014). The alluvial aquifers of NW India have received worldwide attention from past few decades due to the large scale presence of uranium in its groundwater (Coyte et al., 2018).

Punjab is an agriculture dominant state of NW India and major amount of groundwater is employed for irrigation requirements (Kumar et al., 2018). Aquifers in the region are exploited in terms of both groundwater quantity and quality (Bonsor et al., 2017; Baweja et al., 2017; CGWB, 2017b; MacDonald et al., 2016). Although various studies have been carried out on distribution of uranium in the groundwater of Punjab (Bajwa et al., 2015; Coyte et al., 2018; Pant et al., 2017; Rishi et al., 2017; Singh et al., 1995; Singh and Kishore, 2010; Saini et al., 2016; Sharma et al., 2017), however, work done is very limited in the Barnala district which shows highest groundwater depletion (Sidhu et al., 2021). Current study is important as explained studies on vertical extent of uranium contamination are limited in the region. Due to aforementioned, main objectives of this study are to (a) Know the groundwater quality and vertical extent of uranium contamination (b) link the presence of uranium and water geochemistry by utilizing hydrochemical data (c) understand the source of recharge to the aquifer system by employing environmental stable isotopes and relating it with uranium contamination (d) Study the health risks extent on humans due to uranium ingestion in drinking water. Groundwater being crucial source of water in the region, it is important to understand the levels, source and behaviour of this contaminant. The findings of the current study are going to be useful in understanding the source for future exploration, behaviour of uranium with changing groundwater conditions, for planning remediation and better policy management to reduce the health risk.

2. Material and methods

2.1. Study area

The region forms a part of the Indo-Gangetic alluvial plain and in general, represents a flat topography. It comprises of alluvium and windblown sands. The alluvium is mainly composed of sands of various grades clays and silts and is divided into two parts, newer and older alluvium and is thus heterogeneous in nature in accordance to the mode of deposition by constantly shifting river. Kankar (secondary calcium carbonate) in the form of sheet deposits or in nodular form is met at the depth of 0.75 cm–2 m below the surface. Small sand dunes of varying dimensions and different alignments are observed at a number of places. These dunes can be broadly classified to be of scattered type and do not appear to have any regional linear trend although in isolate parts they do have orientation (CGWB, 2017b).

Study area lies in the south part of Satluj River in the Malwa region of Punjab and lies in the arid & semi-arid climatic zone (Paul et al., 2015). It includes Barnala district which is bounded by Moga and Ludhiana in the north, Bathinda in the west, Mansa in the south and Sangrur district in the east (Fig. 1). Soil of the region is highly fertile and is under extensive agriculture. Land use map of the region has been provided in Fig. 1 (National Remote Sensing Centre, 2015-16). The climate of the area is described as semi-arid, tropical steppe, and hot. Area receives unevenly distributed normal monsoon and average rainfall of 434 mm and 504 mm respectively (CGWB, 2017a).

The region forms part of both Ghaggar and the Satluj river sub-basin.

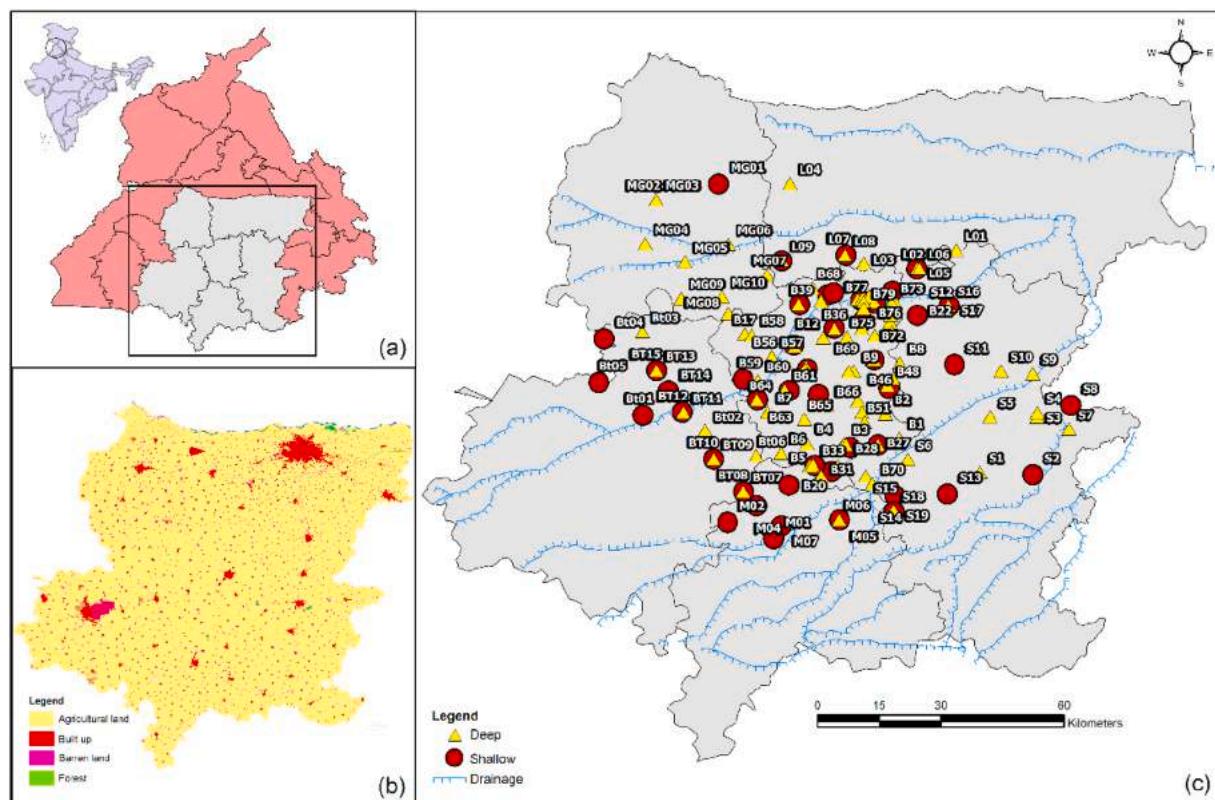


Fig. 1. (a) Location of study area (b) Land use and (c) Sampling sites.

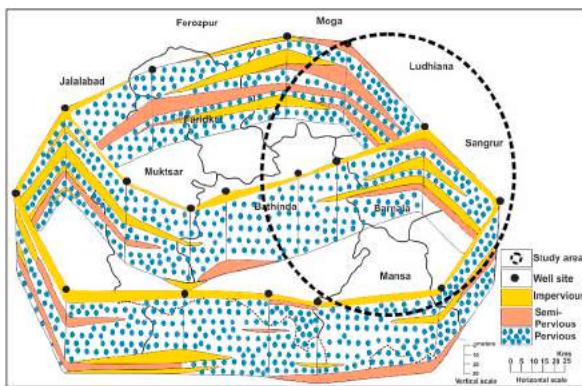


Fig. 2. Lithological Fence diagram of south-west Punjab (modified after Chopra and Krishan, 2014).

Multiple aquifer system exists up to the depth of 300 m with alternate bands of clay and medium-coarse sand. Ground water is in unconfined condition at shallow depth (up to a depth of 60 m) and under semi-confined or confined conditions in the deeper aquifer. Top aquifer is followed by clay bed of 15–35 m thickness and the deeper aquifer extends down to the depth of 300 m. The groundwater is fresh in almost whole district. North-eastern part is more elevated as compared to the south-western part thus reflects the topographic gradient and groundwater flow follows the general slope that is from north-east to south-west (CGWB, 2017a). Lithological cross-section as a fence diagram is shown in Fig. 2 (Chopra and Krishan, 2014).

2.2. Field sampling and analysis

A total of 140 groundwater samples were collected for the post-monsoon season in October–November 2019. Sampling was done on the basis of grid method and samples were collected from every 10 × 10

km grid from the Barnala district and 20 × 20 km grid from the adjoining area. However, there are some variations due to the problems faced in field such as power cuts or unavailability of the required parameters for wells. The water samples were collected from the supply wells used for drinking and/or irrigation purposes. Wells continuously used for water supply were sampled directly after allowing the wells to run for 10 min prior of collection. The samples were labelled properly along with the details of time, place and date of collection. Depth of the wells was obtained from the owner and ranges from 30 to 166 m. All the physical parameters like pH, EC, ORP and temperature were measured in the field in-situ with the help of Hanna Portable meters (HI98120 and HI98121). ORP values presented have been corrected to SHE (Standard Hydrogen Electrode) as the AgCl electrode was used for determination of ORP. The electrode probe for EC and pH were calibrated daily before the analysis. Samples were collected in the 125 ml tarson bottles after filtration through 0.45 µm syringe filter. Samples for the cations measurement and uranium analysis have been preserved by using ultrapure HNO₃. Bottles were prewashed and dried before sampling. Unfiltered water samples were also collected for stable isotope analysis in 50 ml glass bottles and were sealed tightly. The samples were freezed at 4°C until the laboratory analyses were carried out.

2.3. Laboratory analysis

Major cation-anion measurements were carried out at Panjab University laboratory, Chandigarh by using standard methods (APHA, 1995). Sodium (Na⁺) and potassium (K⁺) measurement was done with the use of flame photometer. Calcium (Ca²⁺) and the total hardness were determined by using EDTA titrimetric methods; magnesium (Mg²⁺) was then calculated theoretically. Bicarbonate (HCO₃⁻) content was measured by using HCl titrimetric method and chloride (Cl⁻) was estimated by using Mohr's argenometric titration (Trivedy et al., 1984). Sulphate (SO₄²⁻), phosphate (PO₄³⁻) and nitrate (NO₃⁻) were analyzed with the use of UV visible spectrophotometer (Spectronic 21D). Ion

charge Balance Error has been calculated and is within the acceptable limit of $\pm 10\%$.

Uranium and stable isotope measurement is done with the help of Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent 8900 Triple Quadrupole) and Isotope-Ratio Mass Spectrometer (IRMS; Thermo Scientific Delta V advantage) respectively at Indian Institute of Technology (IIT), Kanpur. Precision and accuracy were determined by using standard solution as replicates. The overall accuracy of the standard analyzed was $\leq 7.8\%$ for U, $\leq 0.2\%$ for $\delta^{18}\text{O}$ and $\leq 0.3\%$ for $\delta^2\text{H}$, with a precision better than $\leq 2.4\%$ for U, 0.1% for $\delta^{18}\text{O}$ and 0.5% for $\delta^2\text{H}$.

2.4. Health risk assessment

It can be done in terms of radiological toxicity as well as chemical toxicity. As uranium is a radioactive element, radiological toxicity or carcinogenic risk is measured in terms of annual effective dose (D) and Excess cancer risk (ECR) and is calculated on the basis of average life span of people in the region, their consumption of water and uranium activity concentration. It determines the probability of individual to cancer risk due to exposure to carcinogenic hazards. Being a heavy metal, it is necessary to measure the chemical toxicity or non-carcinogenic effects of uranium with target on bone and kidneys mainly. Chemical toxicity risk is evaluated in terms of Lifetime Average Daily Dose (LADD) and Hazard Quotient (HQ).

2.4.1. Annual effective dose (D)

International Commission on Radiological Protection (ICRP, 2008) has given the annual effective dose that represents the health risk to whole human body and is quantified as sum of equivalent doses in all specified tissue and organs of body. It is calculated as (USEPA, 2000):

$$D (\mu\text{Sv.y}^{-1}) : A \times I \times F$$

A is the activity concentration of uranium and is taken in terms of Bq.L^{-1} and is calculated as measured value of U in $\mu\text{g.L}^{-1}$ multiplied by conversion factor (0.025 Bq.L^{-1}). Annual ingestion i.e. I is taken as 1478.25 L.y^{-1} at the rate of 4.05 L.day^{-1} (HDR, 2009; Jain et al., 1995). F is taken as dose conversion factor obtained as average of dose coefficient of uranium isotopes ^{234}U , ^{235}U and ^{238}U based on ICP, 2008 and is taken as $4.63 \times 10^{-8} \text{ Sv.Bq}^{-1}$.

2.4.2. Excess cancer risk (ECR)

It is estimated on the basis of USEPA standard method (USEPA, 2000a).

$$\text{ECR} = A \times r \times I$$

A is the activity concentration of uranium. r is the risk coefficient of uranium and is taken as $1.19 \times 10^{-9} \text{ Bq.L}^{-1}$. Total exposure or activity intake of uranium per capita i.e. I is calculated as product of daily intake of water which is 4.05 L.day^{-1} for an adult in India (HDR, 2009; Jain et al., 1995) and total days of exposure in average life span (365^*65) of a person (WHO, 2011b).

2.4.3. Lifetime average daily dose (LADD)

It is described as quantity of chemical substance ingested in a day per kilogram of body weight. LADD is calculated in $\mu\text{g.kg}^{-1}.\text{day}^{-1}$ by using the following equation given by USEPA (2005).

$$\text{LADD} = \text{EPC} \times \text{IR} \times \text{EF} \times \text{ED/AT} \times \text{BW}$$

Exposure point concentration of uranium i.e. EPC is measured in $\mu\text{g.L}^{-1}$. IR is the ingestion rate of water and is 4.05 L.day^{-1} ; Exposure frequency (EF) is taken as 350 days.y^{-1} (USEPA, 1991); ED is the duration of exposure i.e. the life expectancy of a person and is 65 years (WHO, 2011b); AT and BW is the average time in days ($365^* 65$) and average body weight of Indian person (51.5 kg) respectively (Dang et al.,

1994).

2.4.4. Hazard Quotient (HQ)

It is used to estimate the harm extent by using following equation (USEPA, 2005)

$$\text{HQ} = \text{LADD/RfD}$$

RfD (Reference dose) value is given by AERB, 2004 and is taken as $4.53 \mu\text{g.kg}^{-1}.\text{day}^{-1}$.

3. Results & discussion

3.1. Rock-water interaction and hydrochemical facies

Hydro chemical characterization of groundwater using piper trilinear diagram (Piper, 1944) shows that HCO_3^- is the dominant species among anions whereas $\text{Na}^+ + \text{K}^+$ is dominant among cations (Fig. 3) in both the aquifers. It indicates that $\text{Na}^+ - \text{HCO}_3^-$ and $\text{Mg}^{2+} - \text{HCO}_3^-$ are dominant groundwater types in the deeper aquifer whereas shallow groundwater has dominance of Na^+ and Mg^{2+} bicarbonate type of water with $\text{Na}^+ - \text{Cl}^- - \text{SO}_4^{2-}$ type also present in few of the samples. Mixed facies type in the shallow water results from the higher salinity due to evaporation, and mixing of surface and groundwater in the shallow aquifer. The change in groundwater type also varies with the characteristics of groundwater which changes by its interaction with aquifer sediments along with change in direction, flow path and recharge (Singh et al., 2017a).

Groundwater chemistry is also controlled by variety of hydrogeochemical processes taking place in it. To have an insight on these, gibbs diagram were prepared by plotting Total Dissolved Solids (TDS) concentration against ratio of $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ and $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ for cations and anions respectively (Gibbs, 1970). It is seen that majority of the samples fall in the rock dominance zone resulting from interaction of groundwater and aquifer sediments in both the shallow and deeper aquifer (Fig. 4(a) and (b)). Few of the samples also lie in the evaporation dominant zone, signifying the role of evaporation particularly in case of shallow groundwater chemistry.

If silicate and carbonate weathering takes place, bicarbonate ions are usually dominant (Elango and Kannan, 2007). Na^+ vs. HCO_3^- scatter plot (Fig. 4(c)) of current study confirms the same. Rainwater and irrigated water infiltration results in dissolution of silicate & carbonate minerals present along the path and thus bicarbonate and calcium ions are released into the groundwater (Dehnavi et al., 2011). Also, calcium and magnesium ions are dominant than the bicarbonate and sulphate

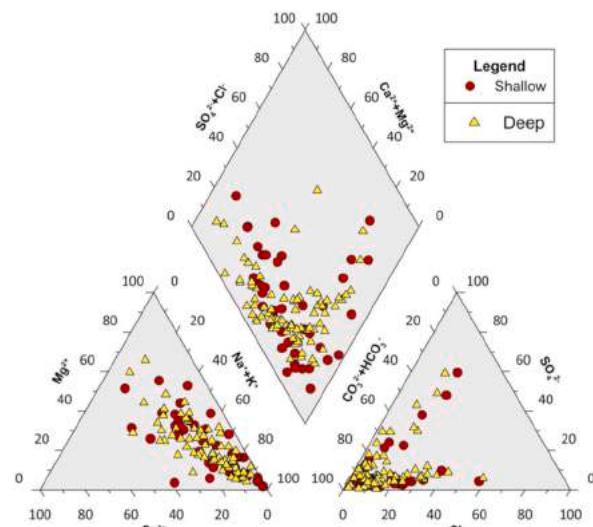


Fig. 3. Piper plots of the groundwater quality parameters.

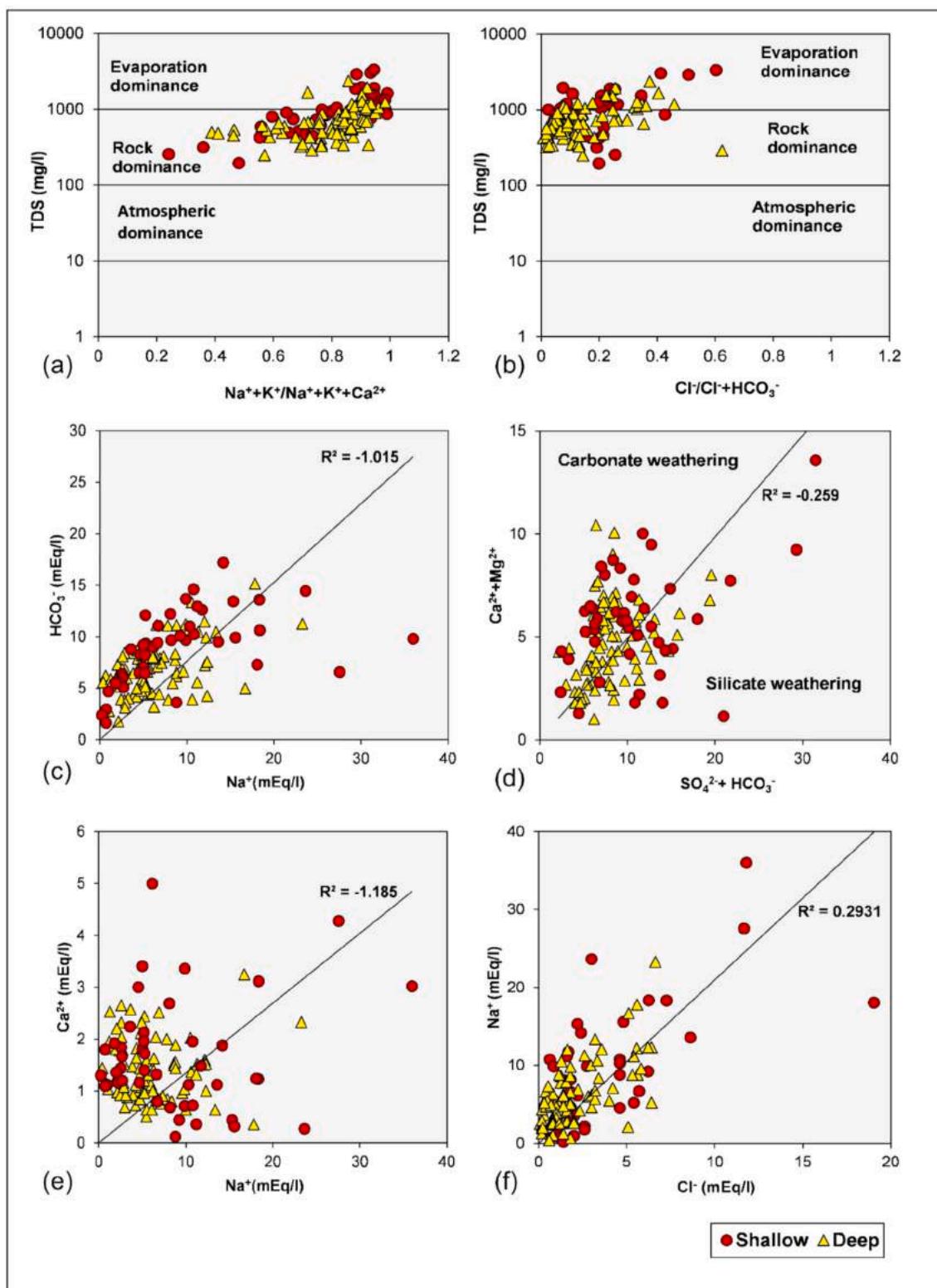


Fig. 4. (a) Scatter plot of TDS vs $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ (b) Scatter plot of TDS vs $\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-$ ratios (c) Plot between Na^+ vs. HCO_3^- (d) Plot between Na^+ vs $\text{Ca}^{2+} + \text{Mg}^{2+}$ (e) Scatter plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{SO}_4^{2-} + \text{HCO}_3^-$ (f) Plot between Na^+ vs Cl^- .

ions in the current study, with majority of samples lying above the equiline as shown in the scatter plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ (Fig. 4(d)). It shows that Ca^{2+} and Mg^{2+} are dominant under the influence of carbonate weathering. Samples close to the equiline shows dissolution of Calcite, dolomite or gypsum (Singh et al., 2017a,b). Few of the samples falling below the equiline show ion-exchange in the

silicate weathering zone, from albite and bicarbonate. Calcium content in the groundwater has increased from the $\text{Ca}^{2+}/\text{Na}^+$ ion exchange as shown in Na^+ vs. Ca^{2+} scatter plot (Fig. 4(e)).

Ionic species in groundwater is also affected by the factors such as evaporation. In Na^+ vs Cl^- plot, samples falling along the equiline show halite dissolution (Fig. 4(f)). In the current study most of the samples

have Na^+/Cl^- value >1 and thus show the dominance of Na^+ ions that may have resulted from the silicate weathering and/or ion exchange processes (Rajmohan and Elango, 2003). However, Na/Cl ratios are greater than what would be expected from mixing between fresh canal water and more saline groundwater. To know the process of ion exchange chloro-alkaline indices are employed (Schoeller, 1977) and negative value of indices indicate that indirect or reverse ion exchange of Ca^{2+} & Mg^{2+} in groundwater takes place with Na^+ and K^+ of aquifer material. The role of reverse-ion exchange processes and carbonate weathering is also observed in the adjoining areas (Kumar et al., 2011; Rishi et al., 2017).

3.2. Hydrochemistry and distribution of ions

Descriptive statistics of the groundwater quality parameters were determined for both the shallow and deep water and statistical summary is given in Table 1 along with the WHO recommended values. Based on the mean concentration of anions also, HCO_3^- is found to be the most dominant anion followed by $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ and among cations Na^+ is found as the dominant cation followed by $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ in both the aquifers. The pH value ranges from 6.95 to 8.27 thus indicating the alkaline nature of groundwater. Electrical conductivity (EC) of the groundwater ranges from 290 to 4970 $\mu\text{S.cm}^{-1}$ and is higher in the shallow groundwater. Higher oxidation-reduction potential (ORP) values are found in the shallow aquifers owing its access to oxygen. In the deeper aquifer, lower ORP values are found in less than 5% samples, representing anoxic conditions, however, in deeper aquifer also oxic conditions are prevalent (Figs. 5–7). The range described is concordant with the value observed by Kumar et al. (2021) in Bathinda, Barnala and Ludhiana; Sharma et al. (2021) in Mansa district, Ahada and Suthar

Table 1
Descriptive statistics of groundwater quality parameters and WHO limit.

Shallow Aquifer						
	Mean	Median	SD	Minimum	Maximum	WHO (2011)
pH	7.46	7.5	0.27	7.05	8.24	6.5–8.5
EC	1649.73	1375	568.68	290	4970	1500
ORP	333.52	346.5	5.91	224	396	—
Na^+	204.50	153	94.21	4.90	827.12	200
K^+	9.31	6.5	2.64	2.70	42.41	30
Ca^{2+}	32.97	27.66	11.53	2.40	100.20	200
Mg^{2+}	52.31	49.21	20.29	9.26	172.05	150
HCO_3^-	540.98	566	149.93	100	1050	300
PO_4^{3-}	0.14	0.04	0.03	0.01	1.03	0.1
NO_3^-	58.07	23.5	68.97	8.80	259.44	50
SO_4^{2-}	99.39	29.11	98.82	5.20	1196.38	250
Cl^-	124.70	71	64.01	22.39	674.50	250
U	85.43	63.2	23.35	4.26	318.03	15

Deep Aquifer						
	Mean	Median	SD	Minimum	Maximum	WHO, 2011
pH	7.51	7.49	0.21	6.95	8.27	6.5–8.5
EC	1105.90	980	1078.22	370	3520	1500
ORP	298.51	310	7.03	92	413	—
Na^+	134.93	114.6	173.95	8.70	534.81	200
K^+	5.74	5.75	8.26	0.10	21.94	30
Ca^{2+}	28.34	26.96	21.32	7.21	65.06	200
Mg^{2+}	41.22	35.92	31.55	6.22	97.46	150
HCO_3^-	427.73	420	216.27	108.73	925	300
PO_4^{3-}	0.23	0.07	0.03	0.01	1.11	0.1
NO_3^-	25.92	19.15	51.20	0.08	112.76	50
SO_4^{2-}	59.70	30.9	233.17	3.05	701.48	250
Cl^-	73.35	52.62	127.98	2.52	234.92	250
U	43.50	36.68	66.40	8.11	129.73	15

Note: All the units are in mg.L^{-1} except pH, EC ($\mu\text{S.cm}^{-1}$), ORP (mV) and U ($\mu\text{g.L}^{-1}$). WHO,

World Health Organization; SD, Standard Deviation; EC, electrical conductivity; ORP, oxidation-reduction potential.

(2018) in south-west Punjab.

Spatial distribution maps and the vertical graphs (Figs. 5–7) shows that concentration of ions is higher in the southern part and shallow aquifer of the region. Climate plays an important role in the increasing concentration towards southern portion. Rainfall decreases in the south-west direction and aridity increases resulting in higher evaporation (CGWB, 2017b; Paul et al., 2015; Sidhu et al., 2021). This leads to the high conductivity and higher ion concentration in the south. Higher concentration observed at shallow depth may have resulted due to the soil mineralization with rapid recharge of water through shallow aquifers along with anthropogenic input whereas source of major ions in the deeper aquifers is lithogenic, resulting from dissolution of rocks & minerals of aquifer sediments. Dissolved ion concentration in the groundwater depends on the aquifer matrix and their solubility (Sarin et al., 1989). Addition of nutrients from mineral fertilizers in farmland areas also increases the EC of shallow groundwater.

3.3. Distribution of uranium

Uranium is among the major contaminants that pose severe health risk to population. Uranium concentration was found to be present in 76% of the water samples higher than the detection limit of World Health Organization (WHO, 2011a), 30 $\mu\text{g.L}^{-1}$. 34% of samples have uranium concentration greater than or equal to the drinking water guideline provided by Atomic Energy Regulatory Board (AERB) of 60 $\mu\text{g.L}^{-1}$. Uranium concentration ranges from 4.26 to 318.03 $\mu\text{g.L}^{-1}$ and is higher at shallow depth. The range described is comparable to the uranium concentration reported by previous researchers in Punjab (Bajwa et al., 2015; Coyte et al., 2018; Pant et al., 2017; Rishi et al., 2017; Singh et al., 1995; Singh and Kishore, 2010; Saini et al., 2016; Sharma et al., 2017) and Barnala (Kumar et al., 2021; Virk, 2019). In present study, it is seen that uranium distribution is not homogenous over the entire area (Figs. 5 and 6) and among all the samples exceeding recommended values, highest concentration is observed in the shallow water of Bathinda district followed by Mansa, Sangrur, Barnala and Ludhiana respectively. In case of deeper aquifer, highest contamination is seen in case of Moga district followed by Sangrur, Bathinda, Ludhiana and Barnala respectively. Uranium levels are reported in all the districts in Table 2.

An increasing trend of contamination is observed moving from north-east to south-west and hotspots are prominent in the southern region. Increase in uranium concentration towards the south-west can be due to the following reasons. In the study region, groundwater flow is towards the low-lying terrain in the south-west direction (CGWB, 2017b; Krishan et al., 2021) and has resulted in higher uranium concentration due to the longer time gap available for water-rock interactions. Increase of uranium concentration along the groundwater flow direction is also observed in the Al-Batin alluvial fan aquifer of south Iraq by Alkinani et al. (2016). Climate also plays an important role in the higher uranium levels; south-west region is comparatively dry due to less rainfall and higher evaporation (CGWB, 2017b; Paul et al., 2015; Sidhu et al., 2021). Higher uranium concentration in the dry climate is also observed by other researchers (Ayotte et al., 2011). Groundwater logging and nearly disrupted cycle of groundwater recharge in the south-west region (PC, 2013) is responsible for increased concentration of uranium in groundwater. As irrigation and drinking water supply is mainly based on canals in this part and there is minimal use of groundwater due to the increased salinity (Krishan et al., 2021). Also the water recharge from unlined canal network and flood irrigation increases the water level in the south-west direction (Baweja et al., 2017) and results in increased redox potential of water with more oxygen content and thus increases the uranium concentration in groundwater because of its higher solubility and mobility in oxidized hexavalent (U(VI)) form.

Uranium concentration levels are also strongly correlated with the depth of wells and concentration decreases with increase in depth. Though precise pattern varies from region to region, usually wells

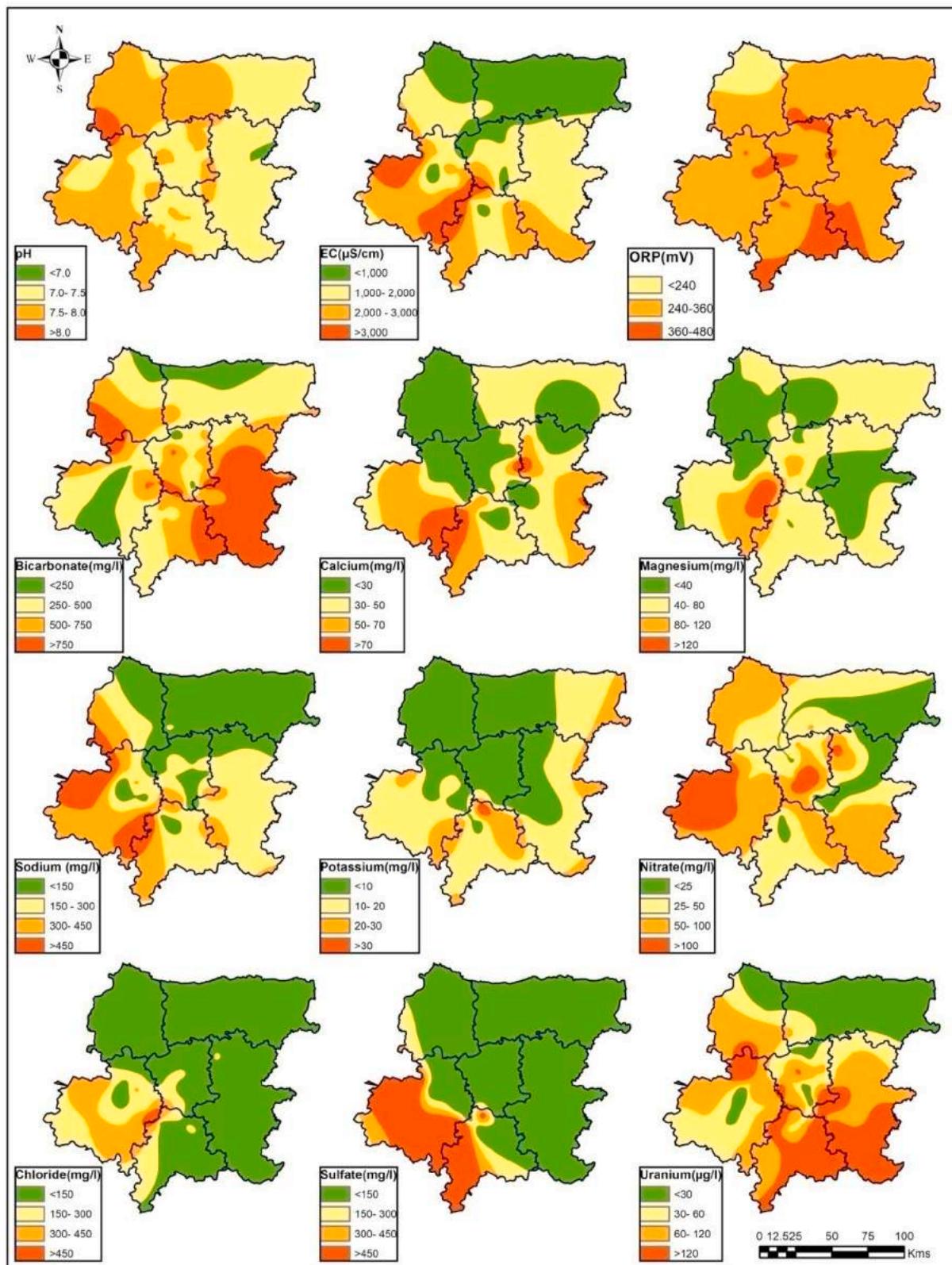


Fig. 5. Spatial distribution of pH, EC, ORP, U and major ions in the shallow groundwater of study region.

deeper than 60 m are less contaminated and higher uranium concentration (>AERB permissible limit) is confined to the shallow aquifer only in the top 60 m. Similar results have also been reported by researchers in south-west Punjab (Saini et al., 2016; Sharma et al., 2017). Anthropogenic inputs such as irrigation return flow (Sahoo et al., 2021), input

from fertilizers (nitrate & phosphate) (Alrakabi et al., 2012; Tripathi et al., 2013) in the shallow water has resulted in higher concentration of major ions such as bicarbonate, electrical conductivity (Figs. 5 and 7) and thus results in increased mobilization of uranium in a way described below.

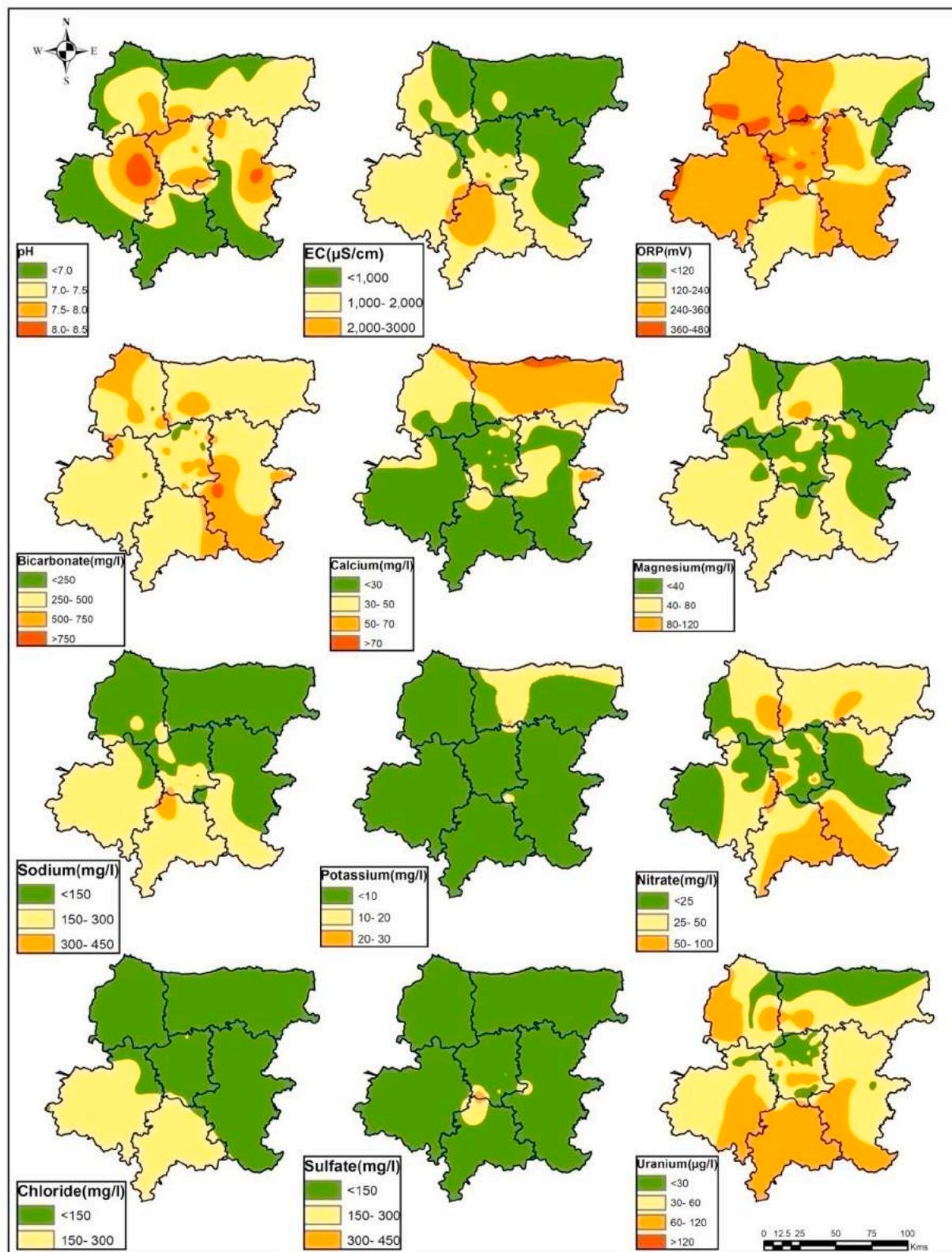


Fig. 6. Spatial distribution of pH, EC, ORP, U and major ions in the deep groundwater of study region.

3.4. Geochemical controls of uranium in groundwater

Uranium in the groundwater may be present from the natural processes or anthropogenic inputs that results in its increased mobilization in the sub-surface (Coyte et al., 2018; Smedley et al., 2006). In the present study uranium in groundwater is predicted from the basic

geochemistry parameters of water. The chemical parameters used in the current study are major ion composition, pH, EC and ORP. Knowledge of groundwater chemistry is essential to understand its influence on the release of uranium from sediments. Data being non-parametric in nature, spearman rank correlation (Table 3) is employed to define the relationship between uranium and other physico-chemical parameters.

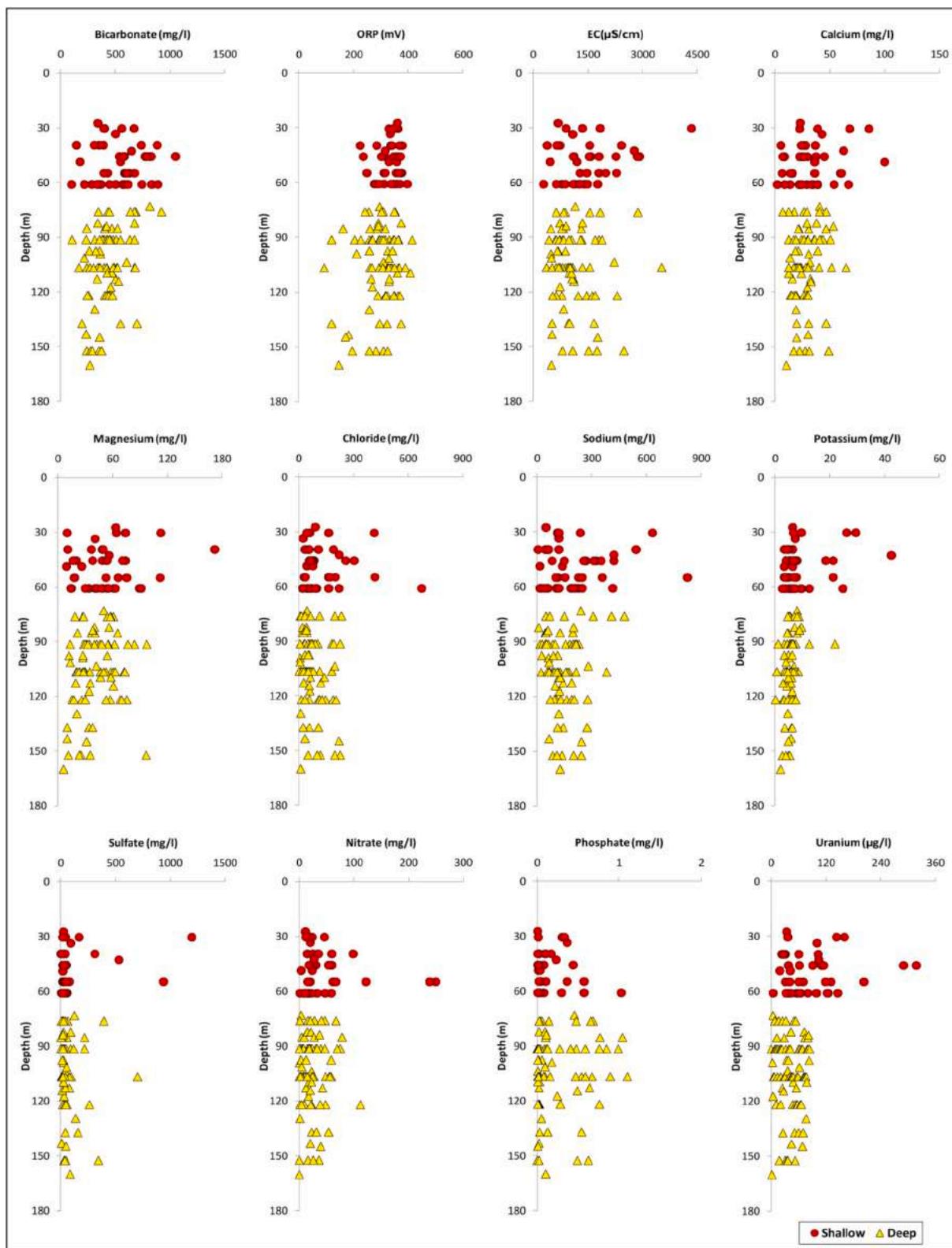


Fig. 7. Vertical distribution of groundwater quality parameters in the shallow and deeper groundwater.

Usually, pH is paramount in governing the dissolution of uranium in the groundwater and affects uranium speciation (Echevarria et al., 2001). Overall pH in the current study is alkaline (>7) and alkaline pH, increases the uranium desorption leading to its dissolution (Wu et al., 2014). Uranium release from soil matrix also depends on the oxidation and reduction reactions taking place (oxidation-reduction potential).

Stable uranium minerals form in the reducing environment (low ORP), causing uranium to precipitate out of the groundwater whereas oxygenated groundwater (high ORP) helps in its dissolution and transportation (Alam and Cheng, 2014; Szecsody et al., 1998). High uranium concentration in oxidizing groundwater of both shallow and deeper aquifer is evident from Figs. 7 and 8. Important role of pH and ORP has

Table 2

District-wise summary of uranium levels in shallow and deep groundwater of study region along with percentage of samples higher than the prescribed limit.

District/Aquifer (no. of samples)		Median	Minimum	Maximum	>WHO limit	>AERB limit
Sangrur (19)	Shallow (7)	91.51	54.61	318.03	100%	86%
	Deep (12)	48.98	26.51	107.86	92%	17%
Barnala (68)	Shallow (19)	41.47	18.78	290.55	84%	37%
	Deep (49)	32.78	8.1	129.72	58%	12%
Bathinda (15)	Shallow (8)	109.11	4.26	204.05	88%	88%
	Deep (7)	43.69	BDL	71.14	58%	14%
Ludhiana (10)	Shallow (3)	36.72	32.28	61.87	100%	33%
	Deep (7)	35.46	25.67	84.88	58%	14%
Mansa (7)	Shallow (6)	104.3	33.89	160.03	100%	84%
	Deep (1)	NA	NA	NA	NA	NA
Moga (10)	Shallow (1)	NA	NA	NA	NA	NA
	Deep (9)	49.41	27.01	102.75	88%	33%

Note: Units are in $\mu\text{g.L}^{-1}$. NA, Not Applicable; BDL, Below Detection Limit; WHO, World Health Organization; AERB, Atomic Energy Regulatory Board of India.**Table 3**

Spearman rank correlation of uranium and physico-chemical parameters in the shallow and deep aquifer of study region.

Shallow Aquifer													
	pH	EC	ORP	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Cl ⁻	U
pH	1.00												
EC	-0.47	1.00											
ORP	-0.13	0.10	1.00										
Na ⁺	-0.34	0.91 ^a	0.01	1.00									
K ⁺	-0.59 ^a	0.41 ^a	0.16	0.35 ^b	1.00								
Ca ²⁺	-0.56 ^a	-0.05	-0.02	-0.13	0.55 ^a	1.00							
Mg ²⁺	-0.31	0.28	0.17	0.01	0.42 ^a	0.16	1.00						
HCO ₃ ⁻	-0.50 ^b	0.69 ^a	0.16	0.75 ^a	0.36 ^b	-0.06	-0.01	1.00					
NO ₃ ⁻	-0.10	0.43 ^a	-0.04	0.35 ^b	0.01	0.04	0.15	0.24	1.00				
SO ₄ ²⁻	-0.27	0.68 ^a	0.14	0.75 ^a	0.32 ^b	-0.05	0.15	-0.52 ^a	0.22	1.00			
PO ₄ ³⁻	-0.61 ^a	0.16	0.17	0.29	0.135	0.27	-0.14	0.27	0.08	0.35 ^b	1.00		
Cl ⁻	-0.07	0.70 ^a	0.06	0.57 ^a	0.29 ^b	-0.10	0.47 ^a	0.31 ^b	0.38 ^b	0.49 ^a	-0.26	1.00	
U	-0.51 ^b	0.80 ^a	0.14	0.84 ^a	0.41 ^a	-0.14	0.07	0.77 ^a	0.14	0.74 ^a	.19	0.52 ^a	1.00

Deep Aquifer													
	pH	EC	ORP	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Cl ⁻	U
pH	1.00												
EC	-0.42 ^a	-0.16											
ORP	-0.16	0.07	1.00										
Na ⁺	-0.07	0.82 ^a	-0.02	1.00									
K ⁺	-0.47 ^a	0.24 ^b	-0.14	0.07	1.00								
Ca ²⁺	-0.61 ^a	0.19	-0.22 ^b	-0.13	0.56 ^a	1.00							
Mg ²⁺	-0.54 ^a	0.43 ^a	0.33 ^a	-0.01	0.37 ^a	0.34 ^a	1.00						
HCO ₃ ⁻	-0.59 ^b	0.58 ^a	0.14	0.41 ^a	0.49 ^a	0.34 ^a	0.59 ^a	1.00					
NO ₃ ⁻	-0.26	0.30 ^a	-0.12	0.19	0.05	0.05	0.32 ^a	0.31 ^a	1.00				
SO ₄ ²⁻	-0.15	0.54 ^a	-0.19	0.71 ^a	0.07 ^b	-0.01	-0.23 ^b	0.12	-0.03	1.00			
PO ₄ ³⁻	0.04	-0.06	-0.52 ^a	-0.02	0.23 ^b	0.39 ^a	-0.14	0.13	-0.05	0.26 ^b	1.00		
Cl ⁻	-0.27	0.73 ^a	0.33 ^a	0.60 ^a	-0.05	-0.10	0.37 ^a	0.17	0.30 ^a	0.21 ^b	-0.48 ^a	1.00	
U	-0.51 ^a	0.49 ^a	0.17	0.41 ^a	0.45 ^a	-0.21	0.48 ^a	0.78 ^a	0.21	0.10	0.02	0.18	1.00

^a Correlation significant at level 0.01.^b Correlation significant at 0.05 level; EC, Electrical Conductivity, ORP, Oxidation-reduction potential.

been considered by Kumar et al. (2011) and Hundal (2011) in adjoining districts. In the current study it is observed that pH and ORP provides favourable conditions for the release of uranium but are not the controlling factors of uranium mobilization because of oxic and alkaline nature of groundwater in the entire region.

U is seen to have positive correlation with electrical conductivity, bicarbonate, sodium and potassium in both the aquifers (Fig. 8, Table 3). It is generally believed that higher the conductance, higher will be the radioactivity of water. Uranium sorption to the sediment decreases with increase in ionic strength because of higher competition among ions in the groundwater. When ionic strength of oxidized solution increases, uranyl ion displacement takes place from the soil exchange sites by other ions such as Ca²⁺, Mg²⁺ and K⁺ and results in its mobilization in high ionic strength solution (Kumar et al., 2014; Krupa et al., 1998; Li et al., 2016). Very strong correlation ($p = 0.80$) of uranium is seen with EC in shallow aquifer and is moderate ($p = 0.49$) in the deeper aquifer. This is consistent with the higher EC value of shallow aquifer due to input from

irrigation recharge, infiltration of rainwater and nutrient addition by fertilisers. Thus greater mobilization is seen in the shallow aquifer and EC has strong effect on uranium mobilization in semi-arid regions. U is strongly correlated with Na⁺ ($p = 0.84$) in the shallow aquifer and is moderately correlated in deeper aquifer ($p = 0.41$), however, the values are comparable in case of K⁺ ($p = 0.41$ & 0.45) in both the aquifers. This shows that liberation of these ions also has effect on uranium mobilization. Leaching and migration of U in alkali matrix is also reported by the Dressen et al. (1982). Strong positive correlation of uranium has also been observed with sulphate ($p = 0.74$) in the shallow aquifer as higher sulphate value is observed in the shallow aquifer and it can act as competing ion for U species (Wu et al., 2018).

In U affected areas, bicarbonate is a major factor controlling uranium mobilization (Langmuir, 1978). In the study region, concordant changes are observed in the uranium-bicarbonate pattern (Figs. 7 and 8) and very strong positive correlation of uranium & bicarbonate has been observed in both the aquifers ($p = 0.77$ & 0.78). Intensive agriculture in the region

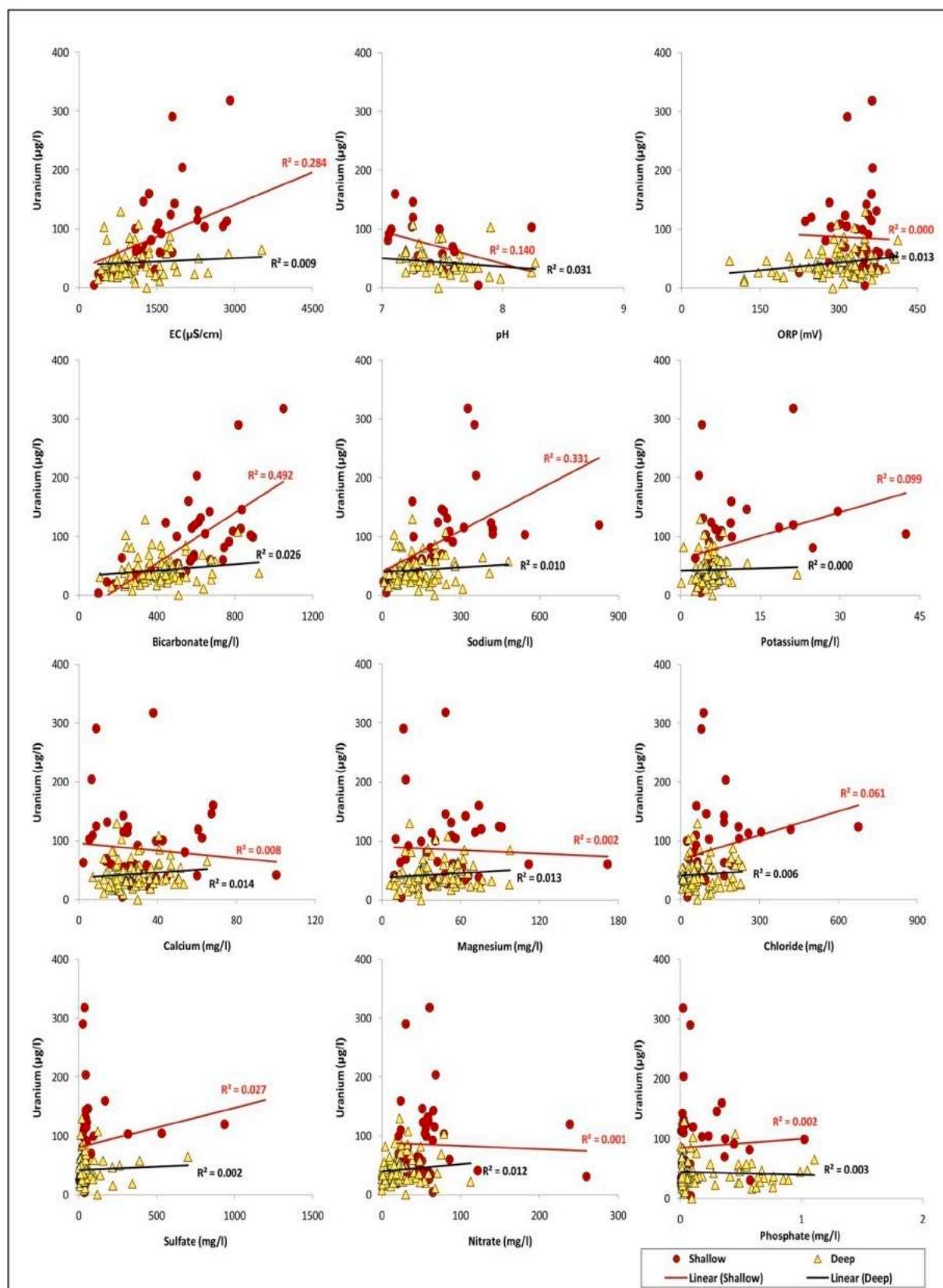


Fig. 8. Association of uranium with basic groundwater parameters.

have resulted in the high bicarbonate present in the groundwater due to plant root respiration that increases the amount of $\text{CO}_2(\text{g})$ in the soil resulting in formation of bicarbonate ions (Rishi et al., 2017). Bicarbonate ions form soluble and stable complexes with uranyl ions that lead to leaching of uranium from the sediments and its migration to long distances (Langmuir, 1997). Uranium mobilization due to the formation of carbonate complexes is known worldwide from the speciation results for similar groundwater environments (Krestou and Panias, 2004; Kumar et al., 2014; Nair et al., 2014; Smedley et al., 2006; Wu et al., 2014). Use of bicarbonate rich groundwater for irrigation also results in higher mobilization of uranium to groundwater (Burow et al., 2017; Jurgens et al., 2008, 2010). Carbonic water percolation through calcareous soils increases its efficiency of leaching uranium from soils. Uranium mobilization in the oxidized groundwater of alkaline pH due to higher levels of bicarbonate has also been reported by researchers from adjoining regions (Pant et al., 2017, 2019; Rishi et al., 2017; Sharma et al., 2017).

3.5. Environmental stable isotopes

Source and mechanism of groundwater recharge was identified by employing stable isotopes and were related with the uranium contamination. Stable isotope content is plotted as $\delta^{2\text{H}}$ and $\delta^{18\text{O}}$ and compared with the reference Global Meteoric Water Line (GMWL) (Craig, 1961). Isotope show wide variation with $\delta^{2\text{H}}$ content lying in the range of -71.12 to -22.77 with an average of -44.31 . $\delta^{18\text{O}}$ content vary from -10.71 to -0.34 with average of -5.37 . All the groundwater samples fall below the GMWL and IMWL indicating the effect of evaporation (Fig. 9(a)). The slope of best fit line indicates that the aquifers get water contribution either from irrigation return flow or from evaporated surface water body. Slope of value less than 8 shows the evaporation effect in groundwater samples (Clark and Fritz, 1997). Precipitation as major source of groundwater recharge and contribution of irrigation return flow in the shallow aquifer is reported by various workers (Kessari et al., 2017; Rao et al., 2017; Sharma et al., 2017). Contribution by canal seepage of depleted isotopic composition (Rai et al., 2014) is also reported by Tripathi et al. (2016). However, less effect of evaporation is seen in the deeper aquifer and is not a case in the current study. There was no significant difference observed in the isotope data of shallow and deeper aquifers, showing the effect of evaporation at both the levels. Thus it shows that some interconnection exists between shallow and deep aquifer, making it susceptible to the anthropogenic impacts.

Recharge and discharge considerably affects the uranium concentration in groundwater (Brindha and Elango, 2013). Water recharge from rainfall increases the water level thus also increases the uranium concentration in groundwater. Recharging fresh water interacts with the uranium enriched soil of the region and results in its dissolution. However, uranium concentration in groundwater starts to reduce due to dilution by continuing recharge of comparatively fresh water. $\delta^{18\text{O}}$ versus U plot in Fig. 9(b) shows that contaminated and uncontaminated groundwater cannot be differentiated on the basis of isotope data.

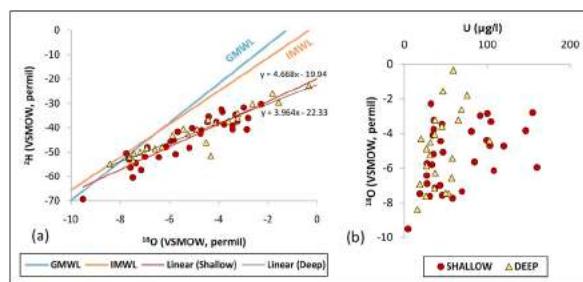


Fig. 9. (a) Stable isotope variation (b) Variation of oxygen content with uranium concentration in both shallow and deeper aquifer.

3.6. Proposed hypothesis for the source of uranium in groundwater

A lot of studies have been carried out regarding the source of uranium in the most affected Punjab state, however, facts are still not clear and requires more work. Research that has been done till date indicate towards geogenic origin of uranium (Patnaik et al., 2016; Singh et al., 2009; Sharma et al., 2018; Tripathi et al., 2013). Current study provides a schematic representation of uranium mobilization from the Siwaliks lying on the north-east of Punjab (Fig. 10(a)). Siwalik sediments are the fluvial deposits along the foothills of Himalayas and are formed of the detritus from sedimentary, igneous, and metamorphic rocks (Krynine, 1937). These granitic bodies have supplied the sediment to form alluvial plains of Punjab lying at foothills of Siwaliks. Primary and secondary uranium minerals are reported from the tertiary and older sedimentary rocks of Siwaliks and are restricted to the uranium mineralized zones (Kaul et al., 1993; Phadke et al., 1985). Siwaliks contributes to the most of groundwater recharge in the region and meteoric origin groundwater is supposed to supply uranium due to the rock-water interactions (Dhanaraju et al., 1985; Welch and Lico, 1998). Uranium mineralization zones of Siwaliks follow the general trend of drainage channels (Rojas, 1989) and oxygenated groundwater percolating through these zones oxidizes and mobilizes uranium from the sediments. When uranium (U (VI)) enriched groundwater moves through former river channels from basin edge to basin centre (Fig. 10(a)), uranium reduction takes place from the water flowing under anaerobic conditions of past time in the favourable environment. Environment with deficiency of oxygen containing less permeable material and reducing agents such as carbonaceous material, hydrogen sulphide and pyrite is considered as the most favourable geologic environment for the uranium ore deposition (Rojas, 1989).

In present day, changing climate and land use have greater role on groundwater uranium concentration. Uranium concentration reaching up to the 10 mg.kg^{-1} is observed in the aquifer sediments of region (Bala et al., 2021). Prevailing oxidizing and alkaline water results in oxidative mobilization of U(IV) from the sediments by interaction with uranium phases (present as secondary minerals or in the form of adsorption). Mobilization is enhanced in the saline water with high bicarbonate resulting from carbonate weathering, high Na^+ and K^+ concentration resulting from the silicate weathering and reverse ion exchange processes from the aquifer sediments. Elevated uranium levels in the shallow groundwater are due to the influence of various anthropogenic activities and addition of water from multiple sources such as canal water, rain water and irrigation return flow. Continuous addition of agrochemicals and recharge of highly ionic irrigation water affects the shallow groundwater (Fig. 10(b)) and results in mobilization of uranium.

3.7. Health risk indices

Health risk assessment is calculated to determine the health effects to the people of malwa region due to ingestion of high uranium water. Human beings are continuously exposed to the uranium via food, soil, air and drinking water. In the study region, drinking water requirements are mainly fulfilled by the use of groundwater. Thus presence of uranium in the water has raised a serious health concern. Punjab has highest number of cancer patients and uranium is considered to be one of the factors causing cancer to the people of the region because of its known carcinogenic effect (Saini et al., 2016).

Cancer risk value in the region varies from 0.12×10^{-4} to 9.09×10^{-4} and AERB has recommended maximum permissible limit of 1.67×10^{-4} for excess cancer risk. Thus in present study 33% of the samples has cancer risk above the permissible limit. Annual effective dose level or Individual Dose Criterion (IDC) due to the water consumption in individual is recommended as 100 μSv.y^{-1} (WHO, 2011b). Current dose level is 7.29 – 544.17 crossing the safe limit.

Lifetime daily dose due to the intake of uranium varies from 0.33 to

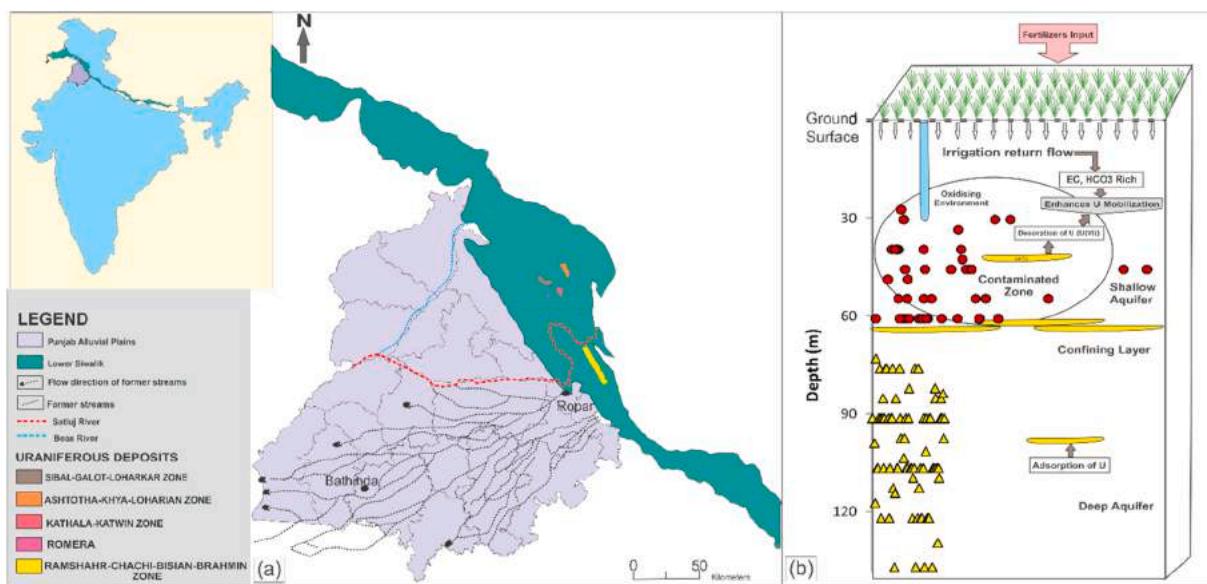


Fig. 10. (a) Uranium Zones in Siwalik (in the Beas-Satluj valley by AMD, IAEA) and former courses of Satluj river in NW India (after Kar, 1999) (b) Schematic diagram of uranium mobilization under present-day conditions.

25.01; contrast in the dose is mainly because of the heterogeneous distribution of uranium in the region. Around 40% of samples have LADD higher than the recommended levels of $4.53 \mu\text{g} \cdot \text{kg}^{-1} \cdot \text{day}^{-1}$ (AERB, 2004). Hazard quotient value also varies from 0.074 to 5.521 and value greater than 1 is not acceptable as far as the chemical toxicity is concerned. Thus groundwater in the region is not safe for drinking purposes with 33% of samples exceeding the safe limit.

4. Conclusion

This study investigates the occurrence of uranium in the alluvial aquifers of semi-arid Punjab and defines factors controlling uranium enrichment. The key findings of this study are summarized below:

- Study shows that uranium distribution is not homogenous throughout the region, however, spatial distribution graphs reveal that concentration increases towards south-west direction. Factors such as regional groundwater flow, high groundwater table due to water logging, extensive use of canal water and higher evaporation in the semi-arid south-west portion controls the enhanced uranium levels in groundwater.
- Hydrochemical analysis shows that major cations & anions concentration is higher at shallow depth along with the high uranium prominent in the shallow zones. EC, HCO_3^- , Na^+ and K^+ are identified as the controlling factors of uranium mobilization in both the aquifers. However, correlation of SO_4^{2-} and Cl^- is seen only in the shallow aquifer and gives indication towards anthropogenic enrichment. Anthropogenic inputs from fertilizers and irrigation plays vital role in the increased uranium concentration of shallow aquifer and cannot be ignored.
- Carbonate weathering is the dominant hydro-geochemical process controlling groundwater chemistry and strong correlation of uranium with electrical conductivity and alkalinity imply that weathering of carbonates and desorption of uranium from mineral surface is major cause of uranium mobilization in the aquifer system.
- Environmental stable isotopes show the evaporation signature in both the aquifers indicating the contribution of irrigation or evaporated water to the aquifer system. It also shows that a connection exists between the shallow and deeper aquifer and warns against the possible contamination of deeper aquifer in the future.

- Hazard index value exceeds the permissible limit in 33% of the samples and is a potential threat for people residing in the region by posing significant cancer risk.
- As the spatial variability of the uranium contaminated wells is very high, there is urgent need to identify the unsafe wells with large scale testing to reduce health risk. Shallow groundwater of the region is not suitable for domestic or irrigation use due to uranium contamination, however, deep wells are perhaps better option with the effective governance and by preventing mixing of shallow water to the deeper aquifer.
- Though groundwater chemistry helps in basic understanding of uranium behaviour in groundwater, much detailed aquifer sediments study is required to clearly define the source of uranium in study area and is a part of our future dynamics. Hypothesis provided regarding the source of uranium in groundwater will be useful for the future studies in this direction and can be extrapolated to the other semi-arid regions with the similar groundwater conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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1. Professional Qualifications

Degree	Major	Year	University/College/Board	Scholarship
Ph. D	Civil and Environmental Engineering*	1999	Clarkson University, Potsdam, New York, USA	Research Assistantship
M. E	Environmental Engineering [#]	1993	Center for Environmental Studies, Anna University, Chennai	GATE Fellowship & Gold Medallist
B. E	Civil Engineering	1991	College of Engineering Guindy, Anna University, Chennai	First Rank Holder & Gold Medallist

*Ph. D. Dissertation: An Investigation of the Dissolution of Non-Aqueous Phase Liquids (NAPL) in Heterogeneous Porous Media

2. Professional Experience

Period	Title
July 2012 – till date	Associate Professor Department of Civil Engineering, Indian Institute of Technology Madras,
June 2005 – June 2012	Assistant Professor Department of Civil Engineering, Indian Institute of Technology Madras,
June 2003 – May 2005	Senior Research Associate and Consultant M.S. Swaminathan Research Foundation, Chennai, India .
January 2000 – November 2002	Post-doctoral Research Associate University of Illinois at Urbana-Champaign, IL, USA .
October 1993 – July 1994	Design Engineer Larsen & Toubro Inc., ECC, Manapakkam, Chennai, India .

3. Awards/Honours/Merit

Sl. No.	Recognition	Agency/ year
1.	Magudam Award	Science and Technology Category, CNN New 18 / 2017
2.	Gandhian Young Technology Innovator Award (GYTI)	Society for Research and Initiatives for Sustainable Technologies and Institutions (SRISTI), New Delhi, India/ 2015
3	Member (Two terms 2014-2019)	State Expert Appraisal Committee for EIA Ministry of Environment and Forests, GoI
4	Technical Expert Committee Member	Central Pollution Control Board, NCEF Project for remediation of Contaminated Sites 2016 - 2019
5	Expert Committee Member, Solid Waste Management	Chennai Corporation, Government of Tamil Nadu, India 2015- 2018
6	Expert Committee Member, Reverse Osmosis Plants	Chennai Metro Water and Sewerage Supply Board, Tamil Nadu, India 2016
7	Technical expert committee	Kerala State Planning Board for Irrigation projects 2017

4. Research Areas

My research focus has been primarily in the water quality sector - specifically groundwater and industrial wastewater treatment. The major contributions have been under three areas as below - Fundamental research, applied research and my current plans to venture into new arenas.

4.1 Fundamental Research

- Understanding Groundwater Contaminant Transport and Transformations - Miscible pollutants and Non aqueous phase liquids (NAPLs)
- Exsitu and Insitu treatment of heavy metal contaminated wastewater and groundwater
- Developing novel Electrochemical based technologies for removal of micropollutants
- Environmental Microbial Resistance propagation and mitigation strategies

4.2 Applied Research

- Developing industry specific end to end sustainable waste management solutions including minimisation, recovery, reuse.
- Biomethanation, codigestion, Dry digestion, Energy and resource recovery for integrated solid waste management

4.3 Societal Out Reach at Field scale

- Petroleum pipeline spill Contaminated site assessment and Remediation at Tondiarpet
- Pesticide factory site assessment at Srikakulam, Andhra Pradesh
- Field Demonstration Textile Waste water Reuse for agriculture at Ludhiana, Punjab
- Coastal Oils spill investigation and monitoring bioremediation at Ennore
- Restoration of Water bodies of South Chennai - Pallikaranai marsh land and lakes
- Assessment of impact of non engineered dumpsites on groundwater in Perungudi and Kodungaiyur

5 Research Guidance

No of Students/Degree	Graduated	Completing in 2018	Ongoing	Total
PhD	8	4	13	25
MS/M Tech/DD	25	2	2	27
B Tech	10	1		11

6 Projects

Summary of project nos. and funding

Total number of the Sponsored/CSR Projects = 21.
Total value of the Sponsored/CSR Projects = Rs. 21,40,47,700/-

Total number of the Research Based Consultancy Project = 17.
Total value of the Research Based Consultancy Project = Rs. 31,075,656/-

Total number of the Consultancy Project = 25.
Total value of the Consultancy Projects = Rs. 3,800,656/-

Sponsored Projects

No	Title	Sponsoring Agency	Amount	Period
			In Lakh	I R
1.	Surveillance of Environmental AMR and Mitigation of propagation	ICMR	387.00	2018-2023
2.	DST – NERC - EPSRC India-UK Water Quality Research Programme AMR and metals interaction through sensors	DST	392.00	2018- 2021
3.	South India Renewable Energy Innovation Challenge	US Consulate Chennai	53	2016-2018
4.	Accelerated Treatment of petroleum chemical sludge using coupled Physicochemical, Photochemical, and biological processes (UAY)	Ministry of Petroleum, MHRD & BPCL	97.00	2016-2018

5.	Centre for Environmental Technology Dissemination, Demonstration and R&D for Industrial pollution.	TNPCB	500	2013-2017
6.	Evaluation of strategies or the environmental restoration of Pallikaranai marsh	TFDX	5.00	2013-2014
7.	Re-use of waste water (Industry and Domestic) for irrigation in Kancheepuram Municipality	PWD	20.17	2012-2015
8.	The changing risks posed by petroleum hydrocarbons in groundwater environments: Multiphase fluid.	DST/Australia	39.26	2011-2014
9.	Bioremediation of petroleum contaminated site using bio surfactant producers	TNPCB	8.63	2011-2013
10.	Groundwater contamination by organic solvent spills an experimental investigation of the dissolution	DST	10.14	2007-2010
11.	Investigations on the performance of marine coastal collector well	LRAMP Lemelson Foundation	2.28	2007-2008
12.	Up scaling and Parallel Application of Multiple Mass Transfer Correlations to Quantify Dissolution	IITM New Faculty Fund	5.00	2005-2008

7 Research Output

a. Summary of publications

S. No.	Publication Type	Published	Communicated
1	Patents	05	3
2	Chapters in Book	04	
3	Technical articles outreach	6	08
4	Refereed International Journals	124	6
5	Conferences/Symposia	55	

b. Patents

1. Sriram, S., Chetty, R., Nambi, I.M. (2017) Apparatus for removal of metals from wastewater and method there OF, filed for Indian patent on 23.06.2017 [PATENT NUMBER 201741022070]
2. Sriram, S., Chetty, R., Nambi, I.M. (2017) Apparatus for dual phase chromium removal and energy recovery and methods thereof, filed for Indian patent on 30.06.2017 [PATENT NUMBER 201741023125]
3. Nambi, I.M., and Divyapriya, G., "LCD-Graphene electrode and a method of preparation thereof" (Patent No: 2018410000
4. Nambi, I.M., and Divyapriya, G., Srinivasan, R., "A bifunctional rotating drum electrode system for efficient treatment of persistent organic pollutants" (Submitted IDF No.: 1607)
5. Nambi I.M and Albino J, " Isolated a new microorganism which can produce surfactants in anaerobic conditions" Name of the Organism: Pseudomonas sp. ANBIOSURF-1 International Gene Bank NCBI, NIH, U.S.A. Submission: 2009 Accession Number: FJ93009

c. Peer Reviewed International Journal Publications

1. Rosado, D., Castillo, F., Nambi, I., Sadhasivam, R., Valleru, H., & Fohrer, N. (2023). Evaluating heavy metal levels and their toxicity risks in an urban lake in Chennai, India. *International Journal of Environmental Science and Technology*, 1-16.
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Vertical distribution and radiological risk assessment of natural radionuclides in the alluvial soil profile of south-west Punjab, India

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Abstract

Natural radionuclide levels are studied in alluvial sediments upto the depth of 900 cm. Eighteen profiles are selected from agricultural and undisturbed areas and analysed by gamma-ray spectrophotometer. Levels were found to vary significantly with depth and higher concentration is observed in agricultural samples till the depth of 600 cm and values are comparable after this depth, indicating role of anthropogenic activities on radionuclide enrichment in agricultural areas. However, value is higher than global average at both sites, indicating their geogenic presence. Elemental ratio and multi-statistical analysis are utilized to assess the behaviour of radionuclides involved. Radiological hazard risk assesment is also carried out.

Keywords Natural radionuclides · Soil profile · Radiological risk assessment · Geogenic and Anthropogenic contaminants · South-west Punjab

Introduction

Radioactivity either natural or man-made is ubiquitous in the Earth's crust though in different amount. Human beings are continuously exposed to natural radiation from air, food, ground, building materials and the universe [1]. Natural radionuclides in the soil form significant component of radioactivity and originates mainly from the uranium (^{238}U) - thorium (^{232}Th) decay series and potassium (^{40}K). This component of natural radioactivity depends primarily on mineralogy of the bedrock and also secondary products resulting from weathering [2]. The change in distribution patterns of ^{238}U , ^{232}Th and ^{40}K in the soil involves process of soil formation, weathering and various chemical and biological interactions that influence their levels [3].

Mineral content of the sediment and rocks is closely related to the uranium, thorium and potassium content. Th/K elemental ratio is utilized to know about the mineral

assemblage of sediments (light or heavy minerals). When source rocks disintegrate, potassium is rich in the light or rock forming minerals (feldspars and quartz) whereas most of the uranium and thorium remain associated with the dark or heavy mineral assemblage, that is in accessory minerals. Radionuclides are incorporated in the crystal lattice of minerals during their formation and are transported as such in various heavy minerals [4].

Uranium and thorium migrate under the surface soil conditions and the ability of hydrogenous migration is highest for uranium as it remains soluble for long time and also gets migrated along with the water to long distances [5]. Due to the contrasting behaviour of U and Th, elemental ratio of eTh/eU is used as indicator of the element oxidation or reduction in the sediments. Thorium exists in its insoluble tetravalent form, unaffected by the changing redox conditions and is geochemically associated with uranium. Uranium on the other hand occurs in its insoluble tetravalent form under reducing conditions in the sediments and as soluble hexavalent form in oxidising conditions where it gets mobilized in the solution [6]. Due to the high biological mobility, U-series nuclides have been of particular interest always. Radionuclides with significant mobility are considered as a special group of contaminants in the terrestrial media as they accumulate in the media and enter the food chain [7]. Fast downward moving radionuclides can reach down to the water level contaminating the groundwater

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resources. Thus understanding radionuclide distribution and migration is important part of environmental studies [8].

Distribution of radionuclides in soil also depend on the soil texture, physico-chemical properties of radionuclides, irrigation of land and fertilizer application [9]. Alluvial soil of Punjab is nitrogen deficient and the deficient nutrients are supplied by the common practice of chemical fertilizers application. Radionuclide content is present naturally in the phosphatic fertilisers, derived mainly from the phosphatic rocks [9–11]. Thus cultivation contaminates the agricultural land by inducing large concentration of natural radionuclides present in phosphate fertilizers. Most commonly used compounds in the study region are urea, di ammonium phosphate (DAP), murate of potash (MAP) and complex and single super phosphate (SSP) [12]. The activity concentration is much larger in the MAP fertilizer [13]. Possibility of change in radionuclide levels with land-use and soil heterogeneity is considered in the present study. Thus comparison have been made of agricultural sites with the undisturbed (uncultivated) areas. In recent years, many studies have been carried out to study the behaviour of natural radionuclides in surface soil [14–20]. However, studies are quite scarce on the vertical distribution of natural radionuclides. The study region of Punjab is of interest because of the high uranium levels detected in the aquifer system [21–23]. To better understand uranium distribution patterns in the groundwater of the region, it is highly important to look at the vertical distribution of radionuclides in the soil.

Main objective of the current study is the investigation of vertical distribution of natural radionuclide levels (^{238}U , ^{232}Th and ^{40}K) from agricultural and undisturbed areas of Punjab region. Radiological hazard risk levels has been estimated from the obtained data and are presented. An attempt has been made to understand the leaching and migration of radionuclides by utilizing elemental ratios of nuclides. The study is expected to provide the background data on natural radioactive isotopes for monitoring possible environmental radioactivity pollution in the future.

Materials and methods

Study area

The area selected for investigation is a part of south-west Punjab where high uranium levels are reported in the groundwater [21–23] (Fig. 1). Geologically, it is a part of Indo-Gangetic plain, formed by river sediments through weathering and erosion of igneous or metamorphic rocks from Himalayas. The river laid sediments has developed into the alluvial soil. The alluvium is mainly composed of sands of various grades, clays and silts and is heterogeneous in nature in accordance to the mode of deposition by

constantly shifting river [24]. The area is intensely developed in agriculture, and is affecting the water and soil quality from quite long time.

Soil sample collection for radionuclide measurement

Soil samples were collected from soil cores of eighteen profiles by using a manually oriented hand auger. Auger is attached to the extension rod and lowered down the bore-hole by applying pressure. Auger was rotated to obtain the core of material and after reaching the desired depth, auger was carefully removed from the boring. Auger bucket and rod were cleaned to remove any accumulated soil and steps were repeated for sample collection from deeper depth. PVC (polyvinyl chloride) pipes were used for sampling at higher depth to avoid cross-contamination and any spillage from the upper layers. Sampling depth covered was limited to the depth at which sand began to flow. There are thirteen profiles selected from the agricultural soil (A1-13) and five from the undisturbed soil (U1-5), where there is no agricultural, industrial or urban land use. All the soil cores were drilled down to the depth of 900 cm and sample was collected from each core after an interval of 50 cm, resulting in a total of 300 samples. All the cores reached the depth of 900 cm except three due to the difficulty faced in field during drilling. Samples were packed in the polyethylene bags and coordinates were noted down by using the global positioning system. Samples were carried to the laboratory and dried in the oven at 60 °C for a day or two depending on their moisture content till all the moisture was driven out. Samples were sieved through 2 mm sieve and the texture was noted down.

For radionuclide measurement, each profile was divided into 3 sections on the basis of variation in soil texture, resulting in selection of 51 samples for analysis from all the cores. Sample are labeled as AiDh or UiDh where i refers to the number of soil profile and h (1–3) refers to the corresponding depth interval, 1 is for the depth range of 1–300 cm, 2 for 300–600 cm and 3 for 600–900 cm. A and U denotes the agricultural and undisturbed areas respectively. The depth interval is decided on the basis of texture variation. For the radionuclide measurement, known weights of samples were packed in Petri plates of 75 mm diameter. Containers were sealed tightly and kept aside for more than 30 days so as to attain the secular equilibrium between the parent radionuclides and their daughter products. ^{238}U , ^{232}Th and ^{40}K determination was carried out by using gamma spectrometry at Saha Institute of Nuclear Physics in Kolkata, India. Activity concentration has been noted down in terms of Bq kg^{-1} .

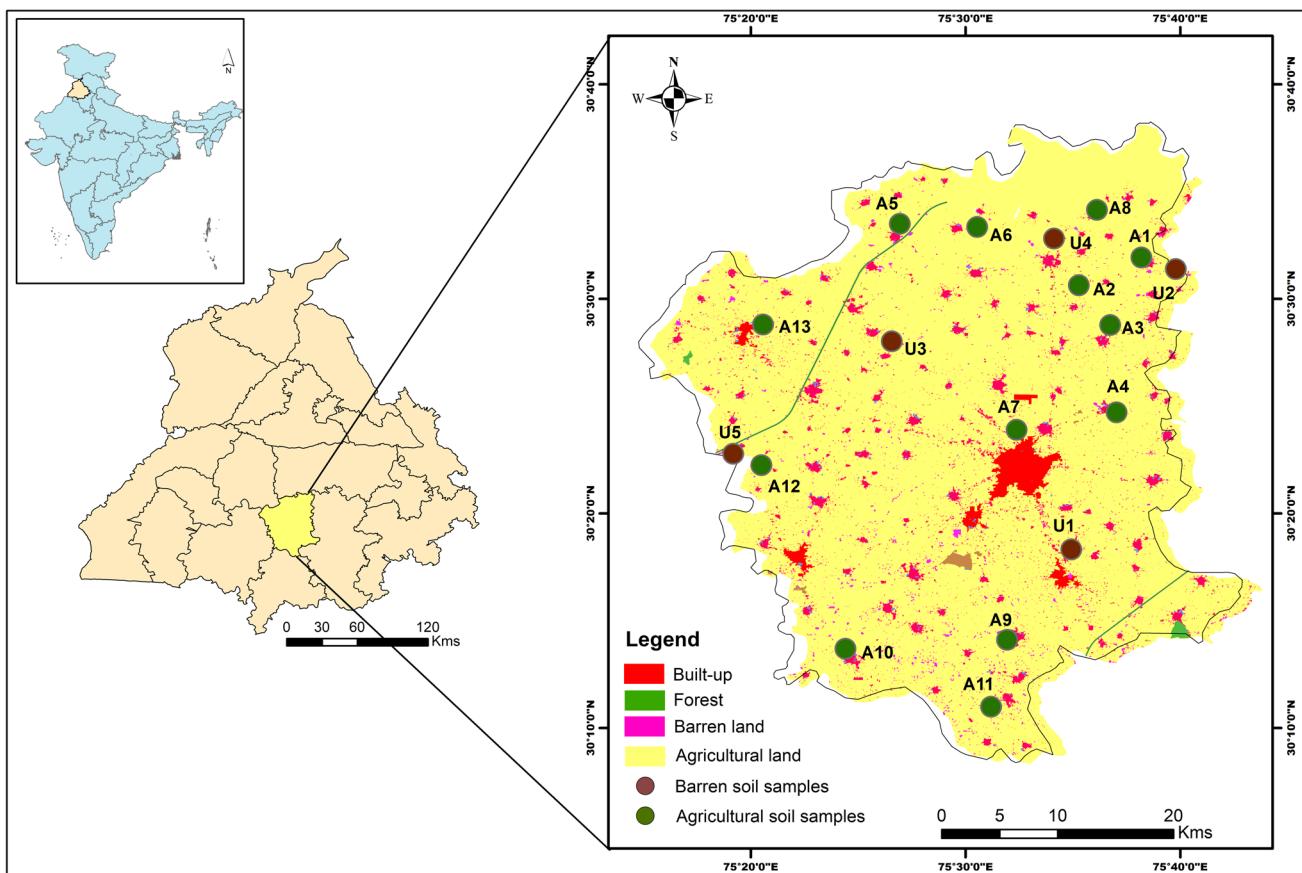


Fig. 1 Location of study area with sampling sites

Instrumentation or calibration and energy lines

All the samples were measured in Canberra model high purity germanium detector (HPGe) with 80% relative efficiency and resolution of 1.65 keV at 1.33 MeV energy. The detector was shielded from background radiation with cylindrical, laboratory lead shield series and was connected with DSA-LX analyser. Energy calibration was performed using ^{60}Co , ^{133}Ba and ^{137}Cs single point sources. Each sample was counted for 60,000 s which was found optimum in the 80% HPGe detector [25, 26]. A Petri-plate filled with SiO_2 was also counted for 60,000 s, which was considered as background spectrum.

The background spectrum was stripped from the spectrum of each sample. ^{238}U and ^{232}Th standards were also prepared from the IAEA RGU-1 (uranium ore) and RGTh-1 (thorium ore) as described in Naskar et al. [26] kept aside to obtain secular equilibrium and were also subjected to measure in 80% HPGe. For measurement of ^{40}K , array of KCl standards were prepared [27]. Gamma energy transition of 295.1, 351.9 keV of ^{214}Pb and 609.1 keV of ^{214}Bi for ^{238}U activity measurement, 338.3, 911.2 keV of ^{228}Ac and 583.2 keV of ^{208}Tl for ^{232}Th [28] and 1460.8 keV for ^{40}K were used.

Activities of ^{238}U , ^{232}Th and ^{40}K has been calculated in the measured samples using comparator method [29].

Radiological hazard risk assessment

Absorbed dose rate in air (D)

By the use of measured radionuclide activity, absorbed gamma ray dose rate has been calculated in the outdoor air at height of 1 m using the conversion factors as per following equation [30]. It is assumed while calculation that contribution to the total dose rate from other radionuclides is insignificant such as ^{137}Cs , ^{235}U , ^{87}Rb , ^{90}Sr , ^{138}La , ^{147}Sm and ^{176}Lu .

$$D(\text{nGy h}^{-1}) = [0.462A_{Ra} + 0.621A_{Th} + 0.0417A_K]$$

where A_{Ra} , A_{Th} and A_K represent the activity concentration of ^{238}U , ^{232}Th and ^{40}K in Bq kg^{-1} respectively.

Annual effective dose equivalent (AEDE)

For conversion of absorbed dose rate to annual dose rate, conversion factor of 0.7 Sv G y⁻¹ is applied. Considering 5 h of average time spent by people outdoor, 5/24 (0.2) is taken as outdoor occupancy factor (20%) and calculation is done using the following equation [31]:

$$\text{AEDE - Outdoor} (\mu\text{Sv y}^{-1}) = D \times 8760 \times 0.7 \times 0.2 \times 10^{-3}$$

Radium equivalent activity (Ra_{eq})

It is one of the widely used hazard index to describe the gamma output from samples with different amount of ²³⁸U, ²³²Th and ⁴⁰K. Radium equivalent activity can be calculated by using the activity concentration of uranium (A_{Ra}), thorium (A_{Th}) and potassium (A_K) in Bq kg⁻¹.

$$\text{Ra}_{\text{eq}} (\text{Bq kg}^{-1}) = A_{\text{Ra}} + 1.43A_{\text{Th}} + 0.077A_{\text{K}}$$

Hazard indices (H_{in} and H_{ex})

External hazard index (H_{ex}) gives the radiological suitability of material used in construction i.e. radiation dose given externally by the material used in construction [30]. Internal hazard index (H_{in}) is calculated to determine the internal exposure to gamma rays due to the short lived gaseous decay product of ²²⁶Ra i.e. ²²²Rn which is carcinogenic and is harmful to the respiratory organs [30].

The equations used for the calculation are given below:

$$H_{\text{ex}} = A_{\text{Ra}}/370 + A_{\text{Th}}/259 + A_{\text{K}}/4810$$

$$H_{\text{in}} = A_{\text{Ra}}/185 + A_{\text{Th}}/259 + A_{\text{K}}/4810$$

Here A_{Ra}, A_{Th}, and A_K represent the activity concentration of uranium, thorium and potassium respectively in Bq kg⁻¹.

Annual gonadal dose equivalent (AGDE)

The gonads (reproductive organs), bone marrow cells and bone surface cells are actively reproducing cells and are more sensitive to radiation than the dormant cells. Thus AGDE due to the specific activity of ²³⁸U, ²³²Th and ⁴⁰K measures the yearly dose equivalent to reproductive organs of population receiving radiation. It can be calculated as described below [32]:

$$\text{AGDE} (\text{mSv y}^{-1}) = 3.09A_{\text{Ra}} + 4.18A_{\text{Th}} + 0.314A_{\text{K}}$$

Elemental ratios

Elemental ratios of eU/eTh, eU/K, eTh/K were calculated to visualise the relative concentration of the radioelements. Elemental activity concentrations are obtained for U, Th and K by using conversion factors as 1 ppm of ²³⁸U by weight is 12.35 Bq kg⁻¹, 1 ppm of ²³²Th is 4.06 Bq kg⁻¹ and 1% of K is 313 Bq kg⁻¹ [33]. These give us an indication that whether the concerned radioisotope is enriched or depleted in the studied samples [34].

Statistical analysis

Descriptive statistical analysis was carried out to get single descriptive value for the large data set which makes it easy to look at the entire data set. Correlation analysis was applied to the chemical data to understand the strength of association and mutual relationships between the variables. All the statistical data processing was carried out with the help of SAS software.

Results and discussion

Distribution of radionuclides

Radionuclide levels of ²³⁸U, ²³²Th and ⁴⁰K for samples have been presented in Tables 1, 2 and Figs. 2, 3. Overall 51 samples were determined for radionuclides, with three samples selected from each profile. Only top samples were selected in the first 300 cm for differentiating the concentration in agricultural and undisturbed areas. However, samples were selected from different depth after this. Natural radionuclide presence is observed in both the agricultural and undisturbed soil samples. It is observed that the distribution is not homogenous throughout the region. From Table 2 and Fig. 2, we see that higher value of radionuclides is observed in the agricultural sites than the undisturbed areas, however, variation is observed only up to the depth interval of 600 cm. The values are comparable after this and are almost similar for D3, 600–900 cm depth. Reported higher levels of radionuclide in the agricultural land indicate role of anthropogenic activities on radionuclide accumulation particularly use of fertilizers. It is seen that in the top soil concentration of ⁴⁰K is relatively higher than the other radionuclides, with an average of 718.50 and 580.38 for agricultural and undisturbed areas respectively (Table 2), representing largest contribution by ⁴⁰K to the total activity of soil. This is due to the large amount of NPK fertilizers used. The continuous addition of chemicals have increased the original sufficient levels of ⁴⁰K in the agricultural sediment samples (Figs. 2, 3).

Table 1 Sampling coordinates and activity concentration of radionuclides (^{238}U , ^{232}Th , ^{40}K)

ID	Latitude	Longitude	^{238}U	^{232}Th	^{40}K
	N	E	Bq kg $^{-1}$	Bq kg $^{-1}$	Bq kg $^{-1}$
A1D1	30.53	75.64	44.0 \pm 1.49	58.9 \pm 3.85	785.6 \pm 11.71
A1D2			67.5 \pm 4.36	85.5 \pm 6.64	1041.1 \pm 13.43
A1D3			28.9 \pm 0.65	43.7 \pm 2.42	515.3 \pm 9.53
A2D1	30.31	75.58	42.2 \pm 1.63	59.3 \pm 4.01	566.7 \pm 10.09
A2D2			38.9 \pm 0.88	57.2 \pm 1.44	637.3 \pm 10.52
A2D3			41.0 \pm 1.02	55.1 \pm 1.49	702.0 \pm 11.02
A3D1	30.48	75.61	36.9 \pm 2.34	56.7 \pm 1.15	602.3 \pm 10.30
A3D2			36.8 \pm 1.52	51.4 \pm 1.69	603.8 \pm 10.33
A3D3			27.4 \pm 0.81	44.1 \pm 1.46	703.9 \pm 11.05
A4D1	30.41	75.62	38.0 \pm 1.49	55.5 \pm 1.16	640.4 \pm 10.63
A4D2			34.4 \pm 1.01	48.8 \pm 3.80	591.3 \pm 10.29
A4D3			39.4 \pm 0.70	57.9 \pm 3.02	560.6 \pm 10.09
A5D1	30.56	75.45	42.2 \pm 2.48	65.6 \pm 4.28	765.0 \pm 11.63
A5D2			37.1 \pm 2.16	54.4 \pm 6.20	653.9 \pm 10.85
A5D3			29.9 \pm 0.90	44.4 \pm 2.29	655.4 \pm 10.75
A6D1	30.57	75.51	44.7 \pm 2.51	73.1 \pm 0.95	676.1 \pm 10.22
A6D2			114.9 \pm 3.44	192.9 \pm 6.68	485.1 \pm 9.51
A6D3			32.7 \pm 0.74	53.8 \pm 1.85	626.8 \pm 10.59
A7D1	30.40	75.54	36.3 \pm 1.39	66.2 \pm 2.76	904.5 \pm 12.75
A7D2			40.7 \pm 0.70	65.2 \pm 8.02	648.8 \pm 11.62
A7D3			29.0 \pm 2.25	42.8 \pm 2.98	700.1 \pm 10.92
A8D1	30.58	75.59	28.1 \pm 0.80	48.7 \pm 3.49	561.8 \pm 10.37
A8D2			41.6 \pm 0.83	64.2 \pm 2.62	603.0 \pm 11.26
A8D3			38.6 \pm 0.20	56.7 \pm 1.37	716.9 \pm 10.60
A9D1	30.23	75.41	53.5 \pm 2.95	75.9 \pm 2.93	815.4 \pm 11.99
A9D2			49.9 \pm 3.31	74.7 \pm 3.78	824.1 \pm 12.11
A10D1	30.18	75.52	30.3 \pm 1.65	44.1 \pm 1.99	738.2 \pm 11.29
A10D2			34.9 \pm 2.58	53.5 \pm 0.39	678.0 \pm 10.92
A11D1	30.37	75.34	42.8 \pm 2.03	67.7 \pm 4.28	718.2 \pm 11.28
A11D2			58.1 \pm 1.89	89.2 \pm 5.18	659.7 \pm 10.88
A11D3			38.2 \pm 3.70	55.3 \pm 2.69	647.1 \pm 10.74
A12D1	30.48	75.34	49.5 \pm 1.57	60.5 \pm 3.80	812.2 \pm 12.02
A12D2			41.6 \pm 1.78	63.4 \pm 3.22	673.0 \pm 10.97
A12D3			47.9 \pm 2.30	70.1 \pm 3.12	777.7 \pm 11.67
A13D1	30.24	75.53	45.2 \pm 3.13	72.5 \pm 1.42	781.1 \pm 12.03
A13D2			47.6 \pm 2.01	73.9 \pm 5.89	684.4 \pm 11.09
A13D3			34.9 \pm 0.79	50.5 \pm 2.94	756.0 \pm 11.64
U1D1	30.31	75.58	33.0 \pm 1.97	48.8 \pm 4.03	529.5 \pm 9.85
U1D2			39.5 \pm 1.77	62.7 \pm 4.40	560.6 \pm 10.15
U2D1	30.51	75.59	36.1 \pm 1.88	58.9 \pm 3.14	540.0 \pm 9.99
U2D2			28.0 \pm 1.71	44.5 \pm 1.42	547.6 \pm 9.86
U2D3			39.7 \pm 1.16	76.9 \pm 4.76	622.6 \pm 10.46
U3D1	30.47	75.44	43.3 \pm 1.79	68.6 \pm 0.77	518.5 \pm 10.31
U3D2			35.4 \pm 0.43	63.2 \pm 2.32	561.8 \pm 10.06
U3D3			33.7 \pm 0.36	53.5 \pm 3.49	614.8 \pm 10.03
U4D1	30.55	75.57	30.7 \pm 0.88	55.5 \pm 2.78	570.8 \pm 10.10
U4D2			42.0 \pm 0.32	64.5 \pm 0.47	583.0 \pm 10.32
U4D3			45.0 \pm 0.86	64.0 \pm 6	835.4 \pm 12.11
U5D1	30.38	75.32	33.4 \pm 1.58	49.1 \pm 3.28	669.0 \pm 10.84
U5D2			53.9 \pm 3.17	81.9 \pm 4.62	726.9 \pm 11.41
U5D3			40.1 \pm 1.92	60.0 \pm 4.82	721.6 \pm 11.26

A, Agricultural land; U, Undisturbed areas; D1, 1–300 cm depth; D2, 300–600 cm depth; D3, 600–900 cm depth

Table 2 Comparison of mean activity concentration (Bq kg^{-1}) of radionuclides in soil with those from similar investigations in other areas

			^{238}U	^{232}Th	^{40}K	References
Jharkhand, India			53.8	44.2	464.2	[40]
Haryana, India			27.9	34.0	306.9	[41]
Punjab, India			15–27	16–57	266–799	[19]
Ludhiana, Punjab			28.58	50.95	569.59	[14]
World average			35	45	420	[30]
Barnala, Punjab	Agriculture	D1	42.55	62.72	718.50	Present Study
		D2	49.12	74.09	692.94	
		D3	34.60	51.32	661.45	
	Undisturbed	D1	33.12	50.92	580.38	
		D2	46.66	71.27	667.42	
		D3	35.86	54.06	667.93	

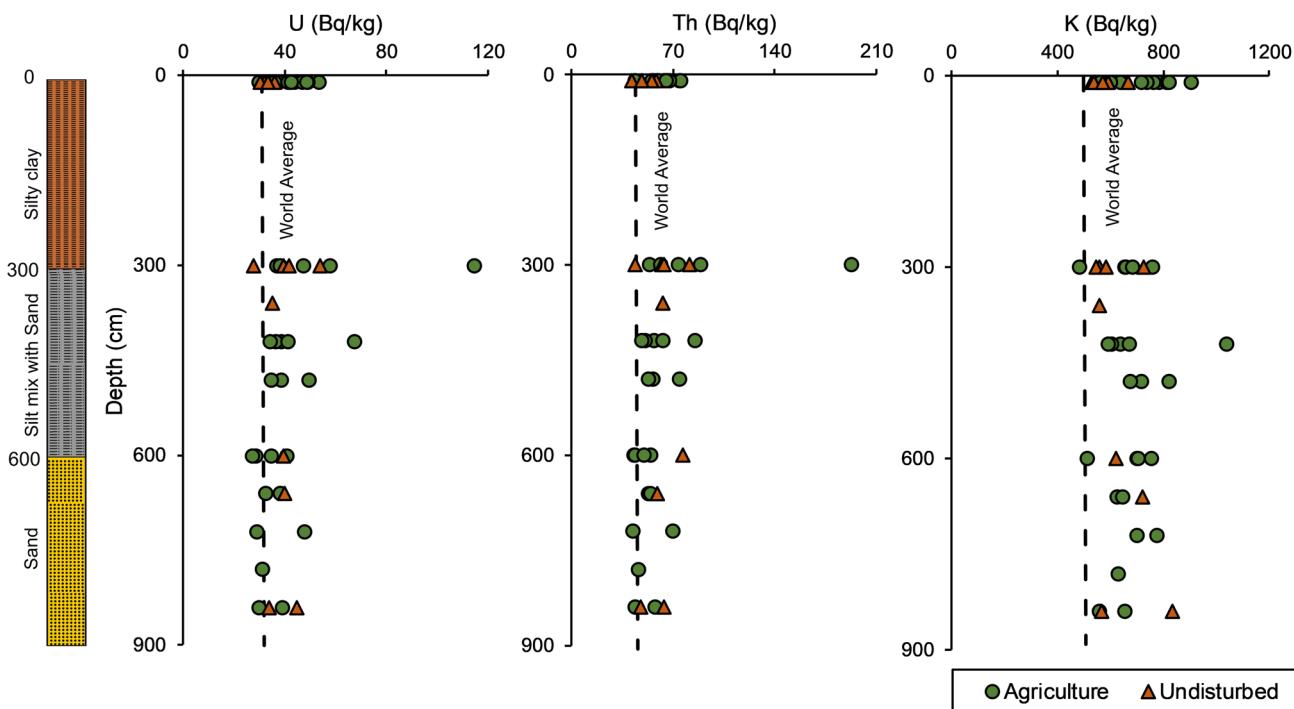


Fig. 2 Vertical distribution of ^{238}U , ^{232}Th and ^{40}K radionuclides along the soil profile in both agriculture and undisturbed areas

There is significant variation of radionuclide levels with depth (Figs. 2, 3; Table 2). Radionuclide content in the soil samples is affected by the number of factors and processes affecting its variability [35]. Variation in concentration with depth in the same profile is due to the different physical, chemical and geochemical properties of the sediments [36]. The soil texture is expected to control the distribution of natural radionuclides [37]. In the study area, clay percentage is found to be higher in the sediments at top and decreases with increasing depth. Radionuclide levels are higher in the finer fraction (clay sediments) due to adsorption of radionuclides in the crystal lattice or on the grain boundaries [38].

Thus high radionuclide concentration points towards more clay content and lower at depth is due to higher sand content. However, exceptionally high concentration of radionuclides at few of the sites does not correlate with the soil texture and marks the uranium accumulation zones in the soil.

It is seen that ^{238}Th and ^{40}K concentration is higher than that of ^{238}U at all the sites (Fig. 3). ^{40}K value is higher because of its chemical composition in clay minerals and thorium by adsorption to clay sediments [39]. Obtained levels from the study area were compared with the data collected by various authors from Punjab, different parts of India and with

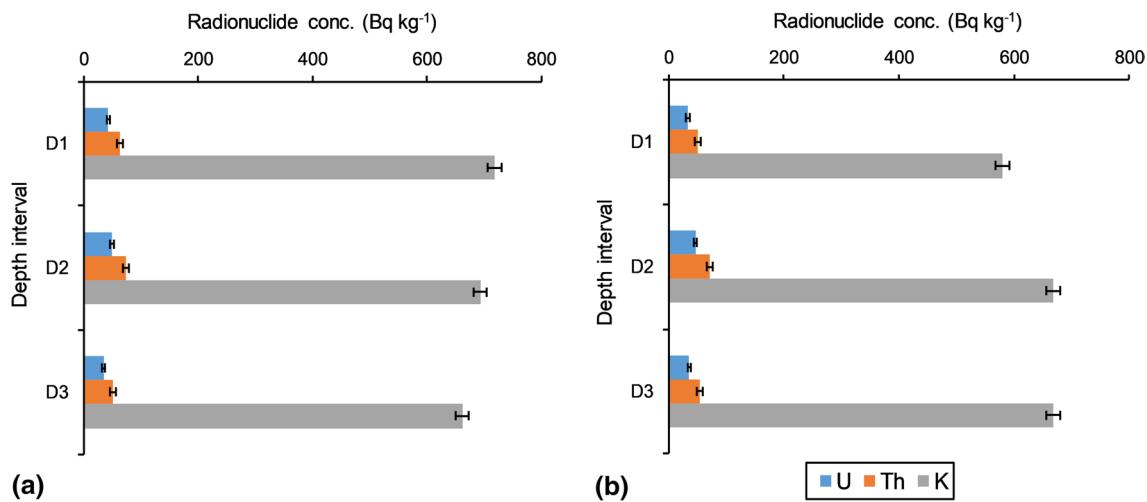


Fig. 3 Natural radionuclide concentration (average) in different sections of soil profile **a** agricultural soil **b** undisturbed areas

international standards (Table 2). It has been observed that more than 60% of samples have levels higher than the Indian average.

Elemental ratios

Th and K distribution

eTh/K ratio shows relative potassium enrichment as an indicator of clay mineral species because both Th (by adsorption) and K (chemical composition) are bound to clay minerals [42]. It is expected that sediment processes do not affect the enrichment or depletion of potassium and thus K acts as radioactive label of the source rock [43]. Calculated Th/K ratio presented in Fig. 4a ranges from 0.0598 to 0.397. High value of K and low eTh indicates that the light

mineral assemblage dominates in the soil samples and it can be interpreted as quartz-feldspar system. However, few samples (A6D2) shows high eTh value and low K, and thus suggests the presence of heavy thorium bearing minerals in the system.

Th and U distribution

Cross-plot of eTh/eU and eTh/K shown in Fig. 4b gives interpretable patterns of the data by giving information about the change in redox potential and change in composition of K [4]. The value obtained for eTh/eU between 3 to 6 and eTh/K between 5 to 10 is consistent with alluvial sediments in oxidising terrestrial environment. This also suggests that this is a quartz-feldspar system with enrichment of clay minerals except few where eTh/K ratio is quite high,

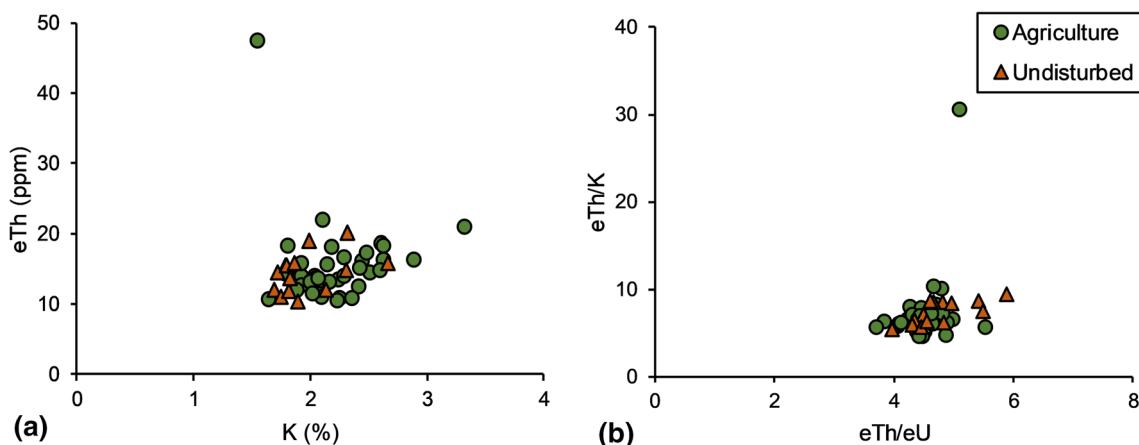


Fig. 4 **a** Correlation between potassium and thorium content in sediment samples **b** Cross-plot of thorium-potassium and thorium-uranium ratios in sediment samples

suggesting quartz-feldspar system with enrichment of clay and heavy thorium bearing mineral association.

eTh/eU value in the sediment samples lies in range of 3.7 to 5.89 with an average value of 4.62, which is higher than the value of average continental crust of approx. 3.8 [44, 45]. This suggests that the samples are enriched in Th(IV) and U(VI). High value of eTh/eU indicates towards an oxidizing environment and thus suggests uranium mobilization through weathering or leaching.

Radiological hazard

Absorbed dose rate in air (D)

The absorbed dose rate in the present study ranges from 61.25 to 189.85 nGy h⁻¹. Average absorbed dose rate value is 84.09 nGy h⁻¹ and is comparable with the world average of 84 nGy h⁻¹ [30]. The maximum average contribution to the total absorbed dose rate is by ²³²Th i.e. 44% followed by ⁴⁰K-34% and ²³⁸U-22%. The change in absorbed rate is due to the spatial variation of mineral holding sediments of that particular element [39].

Annual effective dose equivalent (AEDE)

The calculated outdoor AEDE varies from 75.12 to 232.83 μ Sv y⁻¹ with an average of 103.13 μ Sv y⁻¹. Most of the locations in the region lie in the unsafe region as the value obtained is more than the world average value of 70 μ Sv y⁻¹ [30].

Radium equivalent activity (Ra_{eq})

Ra_{eq} were found to range from 131.11 to 428.17 Bq kg⁻¹ with an average value of 180.76 Bq kg⁻¹. Thus the average value is lower than the world maximum value of 370 Bq kg⁻¹ allowed for public dose and for safe use of material in the building construction [46].

Hazard indices (H_{in} and H_{ex})

Hazard indices are calculated to limit the annual external gamma radiation dose of materials to 1.5 mSv y⁻¹; higher values are harmful to the people living in the region. External hazard index (H_{ex}) value ranges from 0.354 to 1.15 with an average value of 0.49 and Internal hazard index (H_{in}) value for the soil samples lies in the range of 0.43 to 1.46 with an average of 0.59. H_{ex} and H_{in} value of all the samples in the current study lie within the permissible limit and thus poses negligible hazard to the people living in the region.

Annual gonadal dose equivalent (AGDE)

Calculated AGDE range from 0.43 to 1.31 mSv y⁻¹ with an average value of 0.59 mSv y⁻¹. All the sites have value less than unity, which is the limit recommended by International Commission on Radiological Protection for the public [31].

Table 3 Respective minimum, maximum, mean, standard deviation, and range of radionuclides in the agricultural and undisturbed soil samples

	²³⁸ U Bq kg ⁻¹	²³² Th Bq kg ⁻¹	⁴⁰ K Bq kg ⁻¹	D nGy h ⁻¹	AEDE μ Sv y ⁻¹	Ra _{eq} Bq kg ⁻¹	H _{in} mSv y ⁻¹	H _{ex} mSv y ⁻¹	AGDE mSv y ⁻¹
<i>Agriculture</i>									
Mean	42.57	63.57	694.88	87.04	106.75	186.98	0.51	0.62	0.62
Median	39.16	58.44	681.17	81.75	100.25	174.39	0.47	0.58	0.58
Std Dev	14.70	24.39	110.30	21.69	26.61	49.65	0.13	0.17	0.15
Range	87.52	150.14	555.96	128.60	157.72	297.07	0.81	1.04	0.88
Minimum	27.42	42.78	485.13	61.25	75.12	131.10	0.35	0.43	0.43
Maximum	114.94	192.92	1041.09	189.85	232.84	428.17	1.16	1.47	1.31
<i>Undisturbed</i>									
Mean	37.34	58.61	616.52	78.36	96.10	168.62	0.46	0.56	0.55
Median	35.73	59.47	576.89	76.35	93.64	165.44	0.45	0.54	0.54
Std Dev	6.70	11.61	89.52	12.10	14.84	26.69	0.07	0.09	0.09
Range	25.96	39.62	305.92	42.10	51.64	93.35	0.25	0.32	0.30
Minimum	27.97	42.33	529.48	62.62	76.79	133.73	0.36	0.44	0.44
Maximum	53.93	81.95	835.40	104.72	128.43	227.08	0.61	0.76	0.74

Std Dev, Standard Deviation; D, Absorbed Dose Rate in Air; AEDE, Annual Effective Dose Equivalent; Ra_{eq}, Radium Equivalent activity; H_{in}, Internal Hazard Index; H_{ex}, External Hazard Index; AGDE, Annual Gonadal Dose Equivalent

Multivariate statistical analysis

Descriptive statistics

The list of statistical data (mean, median, standard deviation, range, minimum, maximum) of radionuclides and all the radiological parameters is given in Table 3 for both the agricultural and undisturbed soil samples. The data presented shows variation in the concentration of radionuclides in agricultural and undisturbed areas with minimum value comparable in both the areas.

Pearson correlation coefficient

Study of correlation analysis has been carried out to understand the strength of association and mutual relationships between the variables. Obtained correlation coefficients are given in Table 4 as a linear correlation matrix. It has been observed that there is strong positive correlation coefficient between Th and U radionuclides in both site sediments and radiological parameters. This strong positive correlation is due to Th and U decay series occurring together in nature [47] and it shows that U and Th contribute to the gamma radiation in the soil of the region at both the sites. However, in case of K contrasting behaviour is observed in the agricultural and undisturbed areas. Weak correlation has been observed in case of K and other radionuclides as well as

radiological parameters in the agricultural soil samples and is moderately correlated with radionuclides and strongly with radiological parameters in the undisturbed areas. Thus correlation analysis indicates that the mobility of radionuclides is affected by the sedimentation processes in a different way.

Principal component analysis (PCA)

PCA is a multivariate technique used to identify variables by applying varimax rotation with Kaiser Normalization. By extracting the Eigen values and Eigen vectors from the correlation matrix, number of significant factors and the percent of variance explained by each of them were calculated. It is observed from the PCA that PC1 accounts for 89.59% of total variance in agricultural areas and all the variables have positive projection on PC1. As seen from Fig. 5a, PC1 is heavily loaded on U and Th series associated with all the radiological parameters. PC2 is strongly correlated with the potassium and shows contrast between U and Th (negative projection) and K (positive projection) accounting for 10.03% of total variance. These projections show the authentic behaviour of K and U-Th elements due to their enrichment or low influence of K and can be related to the pre-dominance of K-bearing mineral leaching, because K is geochemically mobile under most weathering conditions [48]. However, in case of undisturbed

Table 4 Pearson coefficient correlation among radionuclides and radiological parameters in the agricultural and undisturbed sediment samples

	^{238}U	^{232}Th	^{40}K	D	AEDE	Ra_{eq}	H_{ex}	H_{in}	AGDE
<i>Agriculture</i>									
^{238}U	1.000								
^{232}Th	0.972	1.000							
^{40}K	0.031	-0.074	1.000						
D	0.979	0.968	0.172	1.000					
AEDE	0.979	0.968	0.171	0.999	1.000				
Ra_{eq}	0.984	0.978	0.128	0.999	0.999	1.000			
H_{ex}	0.984	0.977	0.129	0.999	0.999	0.999	1.000		
H_{in}	0.990	0.979	0.107	0.997	0.997	0.999	0.999	1.000	
AGDE	0.976	0.961	0.194	0.999	0.999	0.998	0.997	0.996	1.000
<i>Undisturbed</i>									
^{238}U	1.000								
^{232}Th	0.844	1.000							
^{40}K	0.661	0.418	1.000						
D	0.948	0.924	0.720	1.000					
AEDE	0.948	0.924	0.720	0.999	1.000				
Ra_{eq}	0.946	0.942	0.684	0.999	0.999	1.000			
H_{ex}	0.943	0.945	0.675	0.997	0.997	0.999	1.000		
H_{in}	0.966	0.929	0.684	0.996	0.996	0.997	0.996	1.000	
AGDE	0.945	0.918	0.731	0.999	0.999	0.997	0.996	0.994	1.000

D, Absorbed Dose Rate in Air (nGy h^{-1}); AEDE, Annual Effective Dose Equivalent ($\mu\text{Sv y}^{-1}$); Ra_{eq} , Radium Equivalent activity (Bq kg^{-1}); H_{in} , Internal Hazard Index (mSv y^{-1}); H_{ex} , External Hazard Index (mSv y^{-1}); AGDE, Annual Gonadal Dose Equivalent (mSv y^{-1})

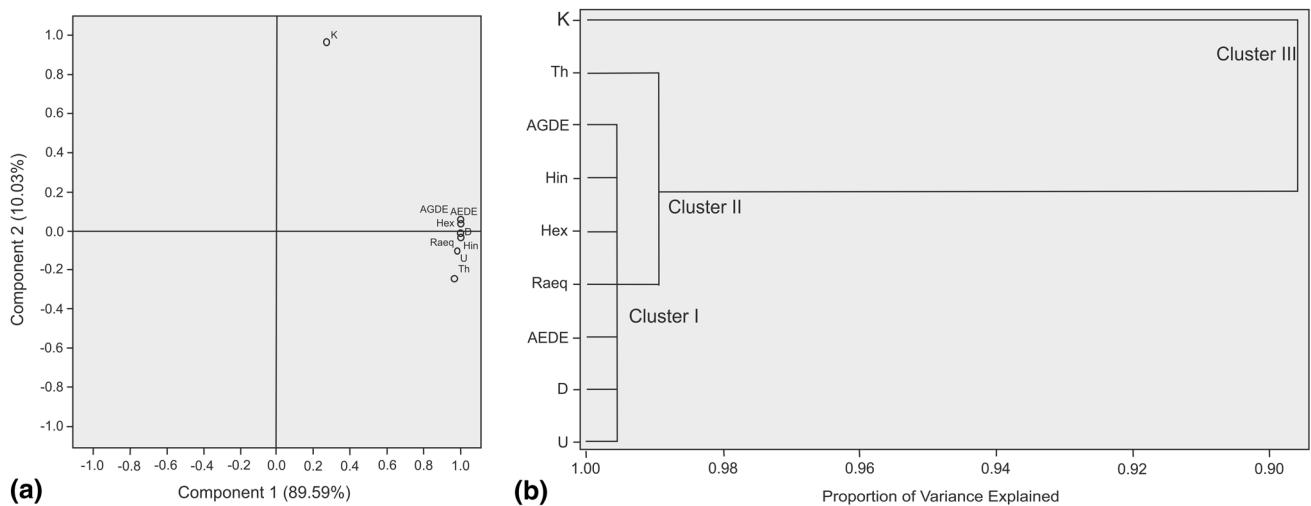


Fig. 5 **a** Principal Component Analysis bi-plot of activity concentration and radiological parameters in samples **b** Dendrogram showing the cluster of variables

samples, only one component forms and no variation is observed. This shows that agricultural activities affect the correlation between radionuclides to a greater extent.

Cluster analysis

Cluster analysis was applied to identify and classify groups with similar characteristics among natural radioisotopes and radiological parameters. This also confirms the existing correlation between variables. Within same cluster, each observation is mostly like others, but all the clusters are dissimilar from each other. Similarity is measure of distance between clusters relative to the largest distance between any two individual variables. Zero percent similarity means clusters are as disparate as least similar region whereas similarity of one hundred percent means clusters are zero distance apart [32].

In the current dendrogram shown in Fig. 5b, all the variables are grouped into 3 significant clusters on the basis of similarity between them. Cluster-I shows correlation of ^{238}U with all the radiological parameters such as AGDE, Hex, Hin, Req, AEDE, D. Cluster-II consists of ^{232}Th and main radiological parameters distribution. Cluster-III accounts for ^{40}K . Cluster analyses suggest that ^{238}U is the major contributor of radiation hazard and ^{40}K does not contribute to any radiological parameters in the agricultural samples of study area. Results corroborate with the PCA and Pearson correlation data as well.

Conclusion

^{238}U , ^{232}Th and ^{40}K radionuclide levels in the soil profile are found to be higher than the previously reported levels and the global average. Levels are higher in the agricultural regions than the undisturbed and the probable cause of difference is the use of high amount of fertilisers as levels are comparable after depth interval of 600 cm at both the lands. However, value is higher than global average even in the undisturbed areas and indicates the geogenic presence of radionuclides in the study region with anthropogenic enrichment. Few of the sites with enhanced uranium levels mark uranium accumulation zones in the soil from where it may get released into the groundwater and can be studied in detail in the future. It is observed that levels are higher in clay sediments at top than the sandy sediments at bottom. Vertical movement of uranium can be traced from the sub-surface sediments through weathering or leaching due to the prevailing oxidising conditions. It shows that soil of the region act as source and sink for uranium with changing redox conditions and counts to be the major factor for the high uranium detected in groundwater of the region.

Various radiological parameters have been calculated, keeping in view that the entire study area is a living place and agricultural region. Sand in the region is also used as construction material thus Ra_{eq} and H_{ex} were calculated to know the radiological hazard. These indices were found to be within the permissible limits, thus posing insignificant radiation hazard and soil can be used safely for construction purposes. However, Annual Effective Dose Equivalent (AEDE) is found to be higher than the world average and poses serious health risk as per its carcinogenic effects are

concerned. Thus there is a need to monitor the radioactivity levels in the future as well.

The data obtained is also important for natural radioactivity mapping and provides the baseline in future to access the environmental pollution due to change in radioactivity levels by any of the nuclear, industrial or human activity.

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Declarations

Conflicts of interest The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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Undertaking by the Principal Investigator

To

The Secretary
SERB, New Delhi

Sir

I Dr. Ritu Bala hereby certify that the research proposal titled "Contrasting distribution of arsenic and uranium in the groundwater of alluvial plains, North India: Implications for origin, fate control, and Health Perspectives" submitted for possible funding by SERB, New Delhi is my original idea and has not been copied/taken verbatim from anyone or from any other sources. I further certify that this proposal has been checked for plagiarism through a plagiarism detection tool i.e. Turnitin approved by the Institute and the contents are original and not copied/taken from any one or many other sources. I am aware of the UGCs Regulations on prevention of Plagiarism i.e. University Grant Commission (Promotion of Academic Integrity and Prevention of Plagiarism in Higher Educational Institutions) Regulation, 2018. I also declare that there are no plagiarism charges established or pending against me in the last five years. If the funding agency notices any plagiarism or any other discrepancies in the above proposal of mine, I would abide by whatsoever action taken against me by SERB, as deemed necessary.

Ritu Bala
09/08/2023

Signature of PI with date

Name / designation

*Dr. Ritu Bala
Ph.D., Panjab University,
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Endorsement Certificate from the Mentor & Host Institute

This is to certify that:

- I. The applicant, **Dr. Ritu Bal** will assume full responsibility for implementing the project.
- II. The fellowship will start from the date on which the fellow joins University/Institute where he/she implements the fellowship. The mentor will send the joining report to the SERB. SERB will release the funds on receipt of the joining report.
- III. The applicant, if selected as SERB-NPDF, will be governed by the rules and regulations of the University/ Institute and will be under administrative control of the University/Institute for the duration of the Fellowship.
- IV. The grant-in-aid by the Science & Engineering Research Board (SERB) will be used to meet the expenditure on the project and for the period for which the project has been sanctioned as indicated in the sanction letter/order.
- V. No administrative or other liability will be attached to the Science & Engineering Research Board (SERB) at the end of the Fellowship.
- VI. The University/Institute will provide basic infrastructure and other required facilities to the fellow for undertaking the research objectives.
- VII. The University/ Institute will take into its books all assets received under this sanction and its disposal would be at the discretion of Science & Engineering Research Board (SERB).
- VIII. University/ Institute assume to undertake the financial and other management responsibilities of the project.
- IX. The University/ Institute shall settle the financial accounts to the SERB as per the prescribed guidelines within three months from the date of termination of the Fellowship.

Dated:



Prof Indumathi M Nambi
Department of Civil Engineering
Indian Institute of Technology Madras

Signature of the Mentor:

Dated:

Signature of the Dean of the Institution