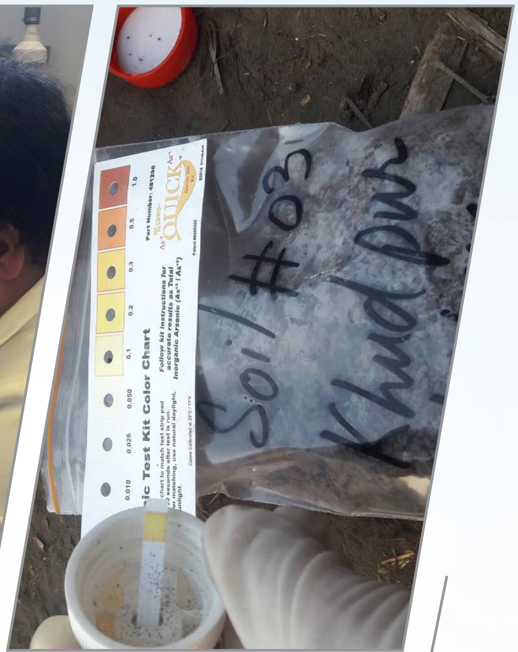
U.S.-Pakistan
Centers for Advanced Studies in Water

Water Conservation and Mitigation of Arsenic in Rice Through Sprinkler Irrigation System

Final Report 2018



Principal Investigator:

Dr. Abida Farooqi, Department of Environmental Sciences
Quaid-i-Azam University Islamabad, Pakistan

Co-Principal Investigators:

Dr. Alexander van Geen, Lamont-Doherty Earth Observatory
Columbia University, USA

Asif Javed, Department of Earth and Environmental Sciences
Bahria University Islamabad, Pakistan

MEHRAN UNIVERSITY
of Engineering & Technology
Jamshoro, Sindh, Pakistan

THE UNIVERSITY OF UTAH

Citation

Farooqi, A., van Geen, A., and Javed, A. (2018). Water conservation and mitigation of arsenic in rice through sprinkler irrigation system. U.S.-Pakistan Center for Advanced Studies in Water (USPCAS-W), MUET, Jamshoro, Pakistan

Authors

1. Dr. Abida Farooqi, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, Pakistan.

2. Dr. Alexander van Geen, Lamont-Doherty Earth, Observatory, Columbia University, USA.

3. Asif Javed, Department of Earth and Environmental Sciences, Bahria University, Islamabad, Pakistan.

ISBN

978-969-23238-5-7

Acknowledgment

This work was made possible by the support of the United States Government and the American people through the United States Agency for International Development (USAID).

Disclaimer

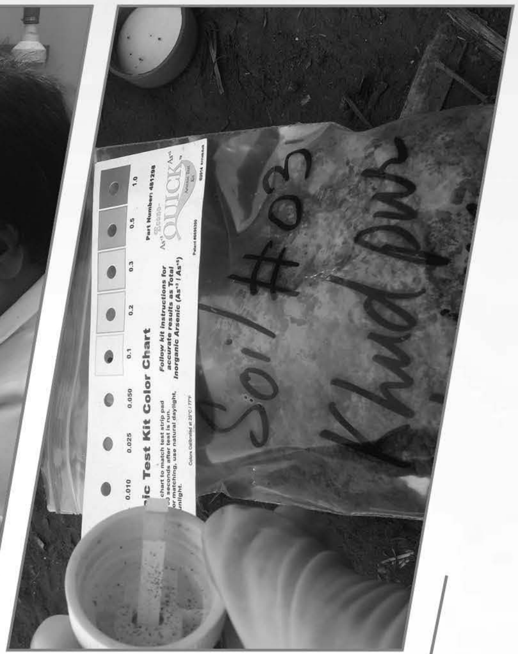
The contents of the report are the sole responsibility of the authors and do not necessarily reflect the views of the funding agency and the institutions they work for.

U.S.-Pakistan
Centers for Advanced Studies in Water

Water Conservation and Mitigation of Arsenic in Rice Through Sprinkler Irrigation System

Final Report 2018





Principal Investigator:

Dr. Abida Farooqi, Department of Environmental Sciences
Quaid-i-Azam University Islamabad, Pakistan

Co-Principal Investigators:

Dr. Alexander van Geen, Lamont-Doherty Earth Observatory
Columbia University, USA

Asif Javed, Department of Earth and Environmental Sciences
Bahria University Islamabad, Pakistan

MEHRAN UNIVERSITY
of Engineering & Technology
Jamshoro, Sindh, Pakistan

THE UNIVERSITY OF UTAH

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

The authors are highly thankful to the United States Agency for International Development (USAID) for funding this project through the U.S.-Pakistan Centre for Advanced Studies in Water (USPCAS-W), Mehran University of Engineering Sciences and Technology (MUET), Jamshoro, Sindh, Pakistan. The authors also acknowledge the Lamont Doherty Earth Observatory (LDEO), Columbia University, New York, USA for extending laboratory support and facilitation for analysis of the project samples.

The authors would also like to thank Mr. Muhammad Munir, resident of Khudpur Village, who gave his land and crop for the experiment. The authors also acknowledge Mr. Tyler Ellis, Laboratory Manager of Lamont Doherty Earth Observatory (LDEO), Columbia University, New York, USA who helped in the analysis of water, soil and rice grain samples at Columbia University. Special thanks are also extended to M. Phil Students, Mr. Zakir Ullah Baig, Mr. Rehman Ashraf who worked tirelessly in the field and also helped in analysis of samples at Hydrogeochemisty Laboratory, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, Pakistan.

We would also like to thank the USPCAS-W authorities for extending administrative support and facilitation for implementing the project plans leading to the successful completion of the project. We also wish to extend sincere thanks to Dr. Kazi Suleman for providing assistance in editing of the report. Lastly, we are thankful to Muzafar Ali Joyo, Graphic Designer for composing and designing this report.

ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
Arsenite	As (III) or As^{3+}
Arsenate	As (V) or As^{5+}
As	Arsenic
BCM	Billion Cubic Meter
Boro	Bengali word means Winter
DMA	Dimethylarsinic Acid
DI	Deionized Water
EC	Electrical Conductivity
EU	European Union
FAO	Food and Agriculture Organization of United Nations
FP	Fundamential Parameters
Ha	Hectares
HFO	Hydrous Ferric Oxide
ICP-MS	Inductively Coupled Mass Spectrometry
IMF	International Monetary Fund
LPS	Litres per Second
l/m	Litre/meter
MMA	Mono-methylarsonic Acid
n	Number of Samples
OM	Organic Matter
ppm	Parts per Million
PCRWR	Pakistan Council of Research in Water Resources
STW	Shallow Tube Wells
XRF	X-Ray Fluoresence
UNDP	United Nations Development Program

EXECUTIVE SUMMARY

Many countries have geological environments that produce groundwater with high arsenic content. The arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater under certain conditions. The Indus Plains of Pakistan, formed by the River Indus and its tributaries, is one of the regions where alarming levels of arsenic concentrations in groundwater have been observed. The high concentrations of arsenic in groundwater combined with the installation of high-volume pumping tube wells, has inadvertently led to one of the most serious environmental health hazards of our time. The pumped water induces the transportation of arsenic ions to the soil which may result in gradual accumulation of arsenic compounds in crops grown on such soil. Of particular concern is rice, the staple for billions of people, as it is grown in fields flooded with high quantities of irrigation water. When soil is flooded over prolonged periods of time, it creates an anaerobic environment, which produces a more soluble form of arsenic, which in turn leads to increased arsenic uptake and its accumulation in rice. It is therefore important that preemptive measures be considered to deal with the threat posed by arsenic contamination, while implementing irrigation practices.

To better understand how arsenic in soil and groundwater is affecting the rice crop, a two-year study on arsenic content in the paddy soils of Punjab was conducted. Covering over 60 rice fields spread over an area of 63.76 ha, the study aimed at screening irrigation wells and soil for arsenic in order to predict regional distribution in irrigation wells, while identifying factors which cause the uptake of arsenic from the water to soil and from soil to rice grains. The study also aimed at mitigating the problem by demonstrating how switching from the traditional system of continuous flooding irrigation to a sprinkler irrigation system reduces, to a great extent, the transfer of arsenic ions from soil-to-water-to-rice grains because arsenic occurs in different forms in water and soils, and is more soluble in one form than in the other.

In the first phase of the study, irrigation well water and soils were tested in specified areas using field kits which were later measured by ICP-MS and XRF, respectively, at Lamont Doherty Earth Observatory (LDEO) of Columbia University, New York. We validated this field kit method by comparing ITS Econo-Quick kit As measurements with XRF measurements on 103 soil samples and found good co-relation (R^2= 0.6562) across 1-123 mg/kg range of concentrations. The results showed that the water in the Ravi flood plain has higher arsenic concentration with 65% of the wells exceeding 50 ug/L and 10% exceeding 100 ug/L in contrast to the Chenab and Jhelum plains and the Rachna and Chaj Doabs where arsenic contamination does not exceed 50 ug/L in any of the wells.

The same trend of arsenic contamination was observed in the soil in the Ravi flood plain where about 30% of the soil samples exceeded 15 mg/kg as compared to the Chenab and Jhelum flood plain, where only 4% and 1.5%, respectively, reach the threshold level of 15 mg/kg. However, in individual fields, the arsenic content in soil varies both laterally and vertically, with higher arsenic concentration found in top soil (0-20 cm) closer to the well heads as compared to the outer fields. We also found that on average a well with 100 ug/L supplies 2.81 kg of As per year to the field of 3100 m^2. The results of soil As speciation reveals that As^{5+} is dominant to As^{3+} in the soil samples collected from Ravi flood plain near Lahore whereas As^{3+} is dominant to As^{5+} in soil samples collected from Ravi flood plain near Narowal area. The results of rice grain As, however, clearly suggest that exposure of the Pakistani population to As contained in export quality basmati rice is less of an immediate concern than the continued use of groundwater containing elevated As levels for drinking or cooking. The capability to perform on site analysis of As in soil by ITS Econo field kit would be a major step forward for delineating the As contaminated areas or “hot-spots” where rice production can be stopped and minimize the health risk due to direct ingestion of As in soil by children.

Based on the first-year results, one field with high arsenic levels in irrigation wells in Khudpur near Lahore in the Ravi flood plain area was selected for the next step of the study, and a sprinkler system was installed in the field. The results manifestly demonstrated that despite using the same arsenic-laden water, arsenic concentration in the soil decreased at the end of the rice growing season with the use of sprinkler irrigation as against flood irrigation. More importantly, there was a considerable decrease in the uptake of arsenic in the rice crop with the use of sprinkler irrigation —31% in the roots, 12% in the stem, 15% in the leaves, and about 39% in the rice grain. However, uptake was still observed due to As accumulation in soil by long term use of As contaminated well. The results of soil As speciation round the rice growing season clearly demonstrate that As^{3}+ dominates in flooding conditions whereas As^{5+}dominates when used sprinkler irrigation which is a compelling evidence that uptake of As in rice was reduced by creating aerobic conditions. This happens because, when soil is flooded over prolonged periods, the soluble form of arsenic increases due to the anaerobic environment created which in turn leads to an increase in arsenic uptake and its accumulation in rice. Switching from flood irrigation to sprinkler irrigation creates an aerobic environment wherein arsenic evolves into a more insoluble form thereby limiting its ability for uptake in rice.

Equally important were the findings regarding the conservation of water by the use of sprinkler irrigation. Based on the average amount of water applied to rice, 30% water is saved with the use of sprinkler irrigation compared to the traditional flood irrigation method without affecting the yield of the rice crop. In this study, the As concentration measured in sprinkler-irrigated rice grains is very low as compared to traditional flooding method, thus indicating less bio accumulation effect. Therefore, beyond the intrinsic agronomic advantages, the substitution of continuous flooding irrigation with sprinkler irrigation where it is feasible could significantly reduce concerns about chronic As intoxication in exposed populations.

1. INTRODUCTION

Use of arsenic (As) containing irrigation water is an emerging problem for rice production in several parts of the world as it can supply As to a growing rice crop and lead to long-term soil contamination with As (Dittmar *et al.,* 2010). High concentrations of As in groundwater and installation of several millions of tube wells mainly in South and East Asia has inadvertently led to one of the most serious environmental health problems such as skin cancers, internal cancers (bladder, kidney, lung), diseases of the blood vessels of the legs and feet, diabetes, high blood pressure and reproductive disorders (World Bank, 2005a, 2005b). The major As affected regions are presently found in large delta sand and along major rivers emanating from the Himalayas such as in Pakistan, India, Nepal, Bengal delta, Myanmar, Vietnam, Cambodia and China (Polya *et al.*, 2005; Acharyya and Shah, 2007; Malik *et al.*, 2009; Berg *et al.*, 2010; Chakraborti *et al.*, 2010; Fendorf *et al.*, 2010; Shukla *et al.*, 2010; Thakur *et al.*, 2010; Saha, 2010; He and Charlet, 2013)

The use of ground water for irrigation induces the transportation of As ions to soil (Panaullah *et al.*, 2009; Dittmar *et al.*, 2010). Several field studies conducted in Bangladesh showed that irrigation with As-rich groundwater causes elevated As concentrations in the upper soil layers (Meharg and Rahman, 2003; Hossain *et al.*, 2008; Panaullah *et al.*, 2009). A study conducted by Ali *et al.* (2003) estimated that irrigation with As-rich groundwater introduces 1360 tons of As into paddy soils in Bangladesh each year. Similarly, Dittmar *et al.* (2007) observed that the concentration of As in the topsoil varied across the field, 23 mg/kg was observed in the inlet while it was 11.3 mg/kg at the end of the field. Consequently buildup of As in soil within a canal command area is heterogeneous and in certain parts it can reach to levels which are toxic to rice (Hossain *et al.*, 2008; Panaullah *et al.*, 2009). Therefore, higher As concentrations in the top-soil near well heads compared to outer fields indicate that there is a significant risk for plants grown in areas contaminated with high As compared to areas with lower As concentrations. The issue of As accumulation in soils as a result of irrigation with As-rich water is well recognized; however regarding the question of As uptake by rice crop, a number of conflicting reports have been published. Many scholars suggest that increased As concentration in soil results in increased As concentrations in grain (Williams *et al.*, 2006; Azad *et al.*, 2009; Khan *et al.*, 2009; Zhao *et al.*, 2009; Rahaman *et al.*, 2011; Rauf *et al.*, 2011). However, there are other studies that suggest less conclusive results indicating that As in the irrigation water and soil is not positively correlated with its uptake by plants. Van Geen *et al.* (2006), for instance, argued that despite the accumulation of arsenic in soil and in soil water attributable to irrigation with groundwater containing elevated As levels, there is no evidence of a proportional transfer to rice grains collected from the same sites. The study by Stroud *et al.* (2011) found that concentrations of arsenic in rice grain varied by 2 to 7 fold within individual fields and were poorly related with the soil As concentration. In a field trial, Panaullah *et al.* (2009) observed no correlation between As levels in the grain and soil in 2006 but saw a negative correlation in 2007. Similarly no significant relationships were observed in rice grown in fields irrigated with high and low level of As containing irrigation water in West Bengal, India (Norra *et al.*, 2005).

In addition, accurate and fast measurement of As in soil in the field remains a technical challenge. It can be detected by several conventional analytical techniques such as atomic absorption spectrophotometry (AAS) and inductively coupled mass spectrometry (ICP-MS). But these methods are expensive, involve lengthy procedures of digestion and require trained personnel to run the instrument (ISO, 1995). Another approach to detect As is by carrying out X-ray fluorescence (XRF) spectrometry. XRF spectrometry has been exercised for on-site analysis of major and minor elements in fields such as geochemistry, forensic science and archaeology (Langford, 2005; Shackley, 2011). It has several advantages when compared to other multi-elemental techniques such as the limited preparation required for solid samples, in-situ measurement by field portable (FP) XRF, non-destructive analysis, increased total speed and thorough put and the decreased production of hazardous waste. Field kits, on the other hand, also provide good opportunity for on-site measurements of As and retain these advantages while additionally providing on-site data cheaply. Although, several studies have been conducted evaluating the effectiveness of As test kits in water (Jakariya *et al.*, 2007; Sankaramakrishnan *et al.*, 2008; Watts *et al.*, 2010; George *et al.*, 2012) and also on the performance of FP-XRF as compared to AAS and ICP-MS in case of soil As (Radu and Diamond, 2009; Parsons *et al.*, 2013) there is hardly any study documenting the performance of field kits for measuring soil As. Therefore, we report, to our knowledge for the first time, the use of ITS-Econo-Quick Kit for on-site measurement of soil As through the cross validation by XRF. Clearly, the capability to perform on-site analysis of As in soil by ITS Econo field kit would be a major step forward. The rapid analytical turn-around and the lower cost-per-sample (~$ 0.33) can provide timely support for field decision-making and allows more thorough sampling of an area to map out contamination patterns, assess spatial variation and to delineate contaminated areas or hot-spots. Even in cases where laboratory analysis is required, this kit can be used to rapidly pre-screen samples.

The Indus Plain of Pakistan hosts extensive agricultural production and a population of over 100 million people. On account of a highly arid climate in the Indus Plain, extensive use of groundwater resources for irrigation, involving higher-volume of water pumping with tube wells, is practiced which became popular throughout Pakistan in the

1960`s (Qureshi *et al.*, 2010). The Indus basin represents an extensive groundwater aquifer covering a gross area of 16.20 million hectares. According to a report there are 350,000 private tube-wells with an average capacity of 30 LPS and over 15000 tube-wells with designed capacity of 60-120 LPS. The pumping from these tube wells is approximately 56 BCM which provide 30% of the total irrigation water exclusively to 2.81 million hectares (Qureshi *et al.*, 2010). But water drawn from these aquifers is found to be contaminated with high As in Jamshoro (Baig *et al.*, 2009), Tharparkar (Brahman *et al.*, 2013), Muzaffargarh (Nickson *et al.*, 2005), Malsai (Rasool *et al.*, 2016) and in northern Punjab (Farooqi *et al.*, 2007a; Farooqi *et al.*, 2007b; Sultana *et al.*, 2014). Pakistan Council of Research in Water Resources (PCRWR) also reported the presence of high As (up to 918 µg/L) in ground water of major rice growing districts of northern Punjab, Pakistan (PCRWR, 2014). More recently, blanket testing across 400 villages of northern Punjab on both sides of Pakistan and India border reveals that As concentrations in drinking water are higher in the areas along the Ravi flood plain whereas concentrations were low along Sutlej, Chenab and Jhelum flood plain (HEC/USAID, 2016).

In Pakistan, rice is grown on an area of 2.5 million hectares, with an annual production of 6811 million tons giving an average yield of 2479 kg/ha (GOP, 2016). It is the most important summer cereal crop of Punjab and Sindh provinces, covering 61% and 31% of the total rice area, respectively. Rice is also an important source of foreign exchange earnings, giving about US $ 933 million annually through its export. Pakistan enjoys a near monopoly status in the export of fine aromatic Basmati-rice which fetches a price 3 to 4 times that of the normal coarse varieties and have more demand in the international markets (GOP, 2016). For the first time, Pakistan Council of Research in Water Resources (PCRWR) has conducted the assessment of As in rice growing areas of Punjab, Pakistan and reported As concentration in rice from 0.084 to 0.356 mg/kg (PCRWR, 2014). However, correlation of As in rice with that in irrigation water is still unclear.

Most of the researches discussed above have focused on drinking water which is no doubt a high priority area but the importance of As enrichment in soil and subsequent uptake in rice due to irrigation with As contaminated ground water cannot be ruled out.

The impact of As contaminated irrigation water on the As content of rice is especially important as rice is the major staple food, and it is grown in flooded (reduced) soils which are rich in As. Another additional concern is that As in soil can be toxic to rice leading to reduced yields. Although, extensive research has been carried out in Bangladesh but agro-ecological and hydro-geological conditions; water environment (reducing/oxidizing) and irrigation methods (blending of canal water with ground water etc.), are slightly different from the other south Asian countries. Therefore, results obtained in Bangladesh cannot be applicable to the Pakistan.

According to a recent report by the IMF, Pakistan ranks third in the world among countries facing acute water shortage. Reports by the United Nations Development Program (UNDP) and the PCRWR also warn that Pakistan will become water scarce country by 2025 as its water shortage is reaching at an alarming level. In the face of increasing competition for water for industrial, domestic and environmental sectors, concerns are also being raised about the productivity of water used in agriculture (Kijne *et al.*, 2003).

Therefore, this study was conducted with the following overall objectives:

1. Screening of irrigation wells and soil for As in rice growing areas in order to predict the regional distribution of As in irrigation wells.

2. Assessment of As and other parameters which controls the uptake of As from the water to soil and from soil to rice grains, in order to device a mitigation strategy.

3. Mitigation of arsenic affected field through sprinkler irrigation to reduce the transfer of As from soil to soil-water and from soil-water to the rice plant and the rice grain in As-affected area and the impact of sprinkler irrigation on rice yield grown.

4. Water conservation by growing rice with sprinkler irrigation instead of the traditional flooding.

2. MATERIALS AND METHODS

This study was conducted in two phases; the first phase involved assessment of As in well water, soils and rice. The second one included installation of sprinkler irrigation system in high-As area and its assessment for water saving and mitigation of As problem in rice soils.

Phase 1

The first phase focused on the following objectives:

1. Screening of irrigation wells and soil for As in rice growing areas in order to predict the regional distribution of As in irrigation wells
2. Assessment of As and other parameters, which control the uptake of As from the water to soil and from soil to rice grains, in water, soil and rice grains
3. Based on the regional distribution, identify the areas with high As in water, soil and rice grain for deployment of the sprinkler irrigation system in that area.

During this phase of the study, an attempt was made to identify the wells containing As and to define the water environment. The wells containing more than 100 µg/L As were analyzed along a transect, starting from inlet point of the well to the end of the field with equal intervals. Ten soil samples were tested for As concentration from single testing point. All these measurements were carried out in the field and portable field kits were used. Rice samples were also taken from all those fields where rice was grown by using As contaminated water. In addition, water, soil and rice samples were also collected for detailed analysis of As^{+3} and As^{+5} in laboratory. These analyses were carried out in Lamont-Doherty Earth Observatory Laboratory of Columbia University, New York, USA.

2.1 Description of the Study Area

The study area lied in the Chaj and Rachna doab, northern Punjab, Pakistan (Fig. 2.1). 'Doab' is a local word used for land between two rivers. The area of Chaj Doab is bounded by Chenab River in the south-east (SE) and Jehlum River in the north-west (NW) and the Rechna Doab is the area between the Chenab and Ravi Rivers (Fig. 2.1). The area is known as rice-wheat belt with rice production in the summer (Kharif) season and wheat in the winter (Rabi) season (Hassan and Bhutta, 1996). The study area was selected on the basis of previously observed high levels of As in groundwater and the prevalence of shallow tube wells (STW) for irrigation (Farooqi *et al.*, 2007a;

Farooqi *et al.*, 2007b; PCRWR, 2014; Sultana *et al.*, 2014). The soil is tilled only once a year by puddling before transplantation of the seedlings in August. The site includes 60 paddy fields with total area of 63.76 hectares (ha).

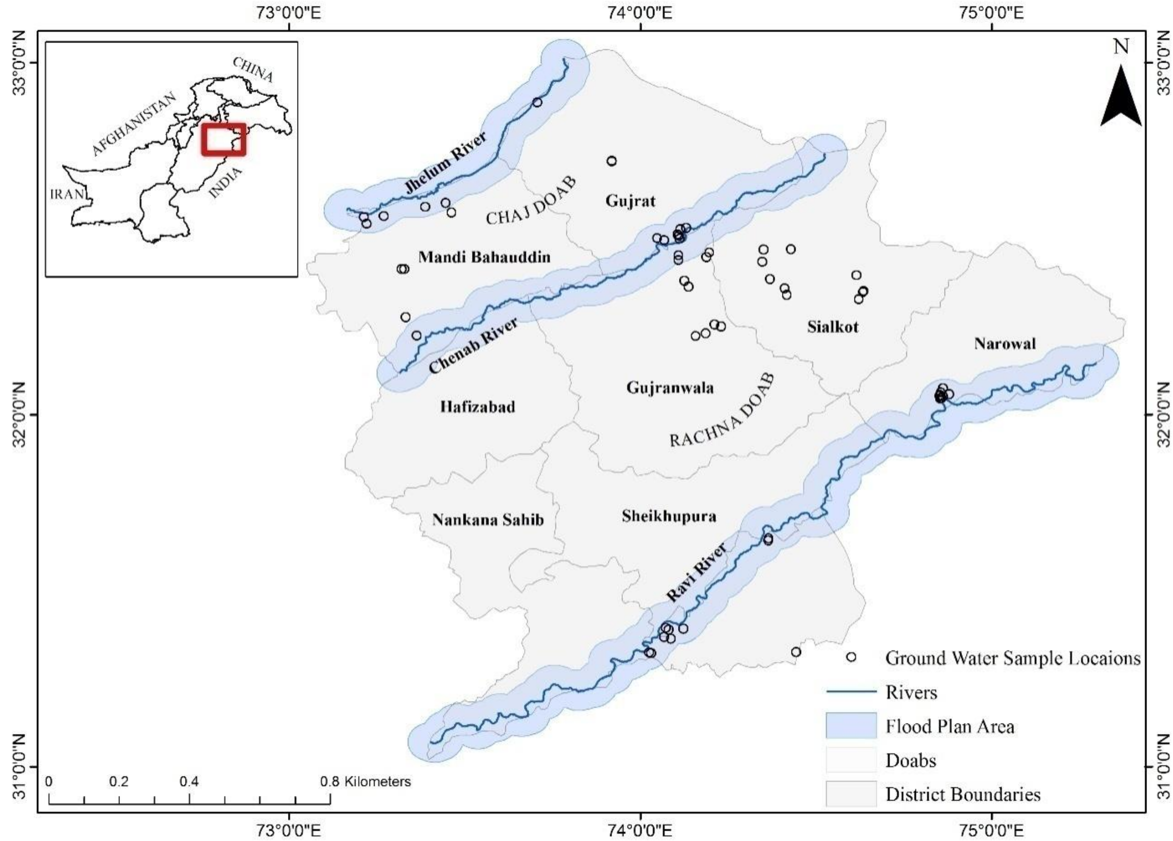


Fig. 2.1: Map of the study area showing water, soil and rice sampling locations, rivers, flood plains, doabs, and district boundaries.

2.2 Soil and Water Sampling

The water and soil sampling strategy was designed in such a way as to detect the variations in As along the three flood plains (Ravi, Chenab and Jhelum) and two Doabs (Rachna and Chaj). Sixty matched sets of irrigation well water and soils were tested from the study area in the field. From each individual rice field irrigated by single well, 10 soil samples were tested along a diagonal (Fig. 2.2). Soil profile sampling (up to 60 cm depth) was restricted to only 10 rice fields in Ravi flood plain with a high As concentration near the well. Soil core samples were collected at six different depths (0-10, 10-20, 20-30, 30-40, 40-50, and 50-60 cm) using a locally made stainless steel core sampler of diameter 2.5 inches (6.35 cm) and length 70 cm. A total of 60 water and 660 soil samples were analyzed in field by the methods described in the subsequent section. The same well water and 103 selected soil samples out of total 660 tested in field were also collected for laboratory measurements. Well water samples were collected in 20 ml polyethylene scintillation vials with a poly seal-lined cap (Wheaton no. 986706) whereas soil samples were collected in polyethylene bags. Rice grain (export quality basmati polished rice) samples were also collected from individual farmer's fields in polyethylene bags.

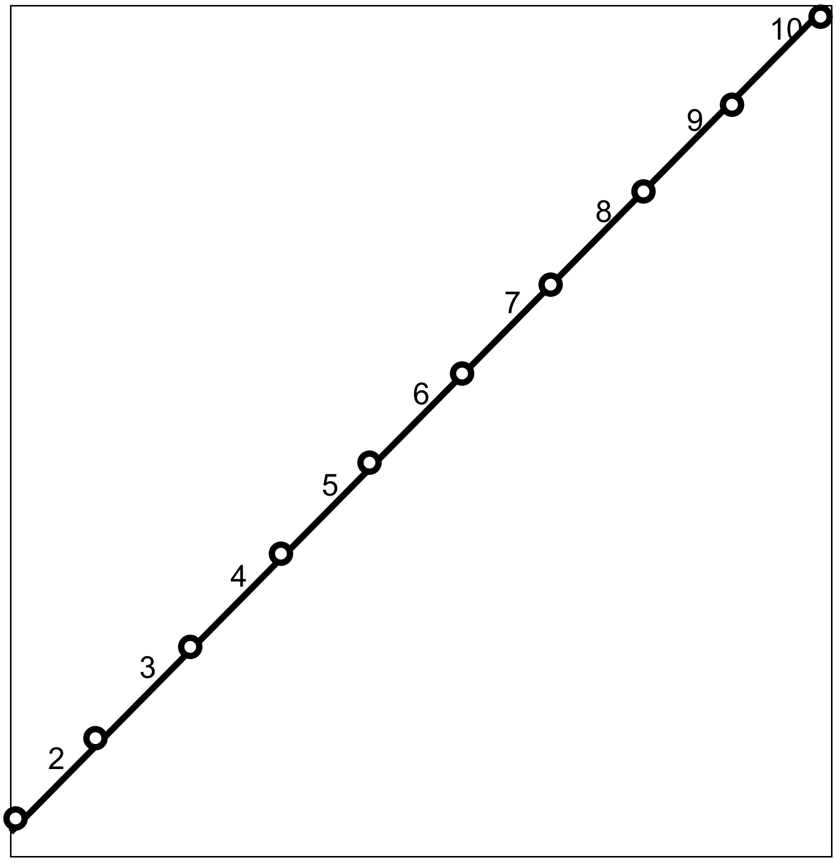


Fig. 2.2: The sequence of soil sampling at individual rice fields.

2.3 Sample Analysis

2.3.1 Field method for screening of irrigation wells and soils for arsenic

Irrigation water samples were analyzed for As using portable ITS As Econo-Quick Kit, which relies on the generation of arsine gas and visual detection on a strip impregnated with mercuric bromide and the standard reaction time was maintained at 12 min. Paddy soils were also analyzed for As using the ITS Econo-Quick field kit; however the procedure was slightly modified whereby 0.5 g soil was mixed with 50 ml of de-ionized water and subsequently treated as water solution. Battery operated weighing balance was used to weigh the soil in the field. Field test results were initially entered in survey CTO (a smart phone application) on the phone which was later uploaded on server. For quality control, the standards of known As concentration (50 and 100 μg/L) were prepared in de-ionized water and tested every day before the commencement of work.

Electrical conductivity (EC) and pH of irrigation wells were determined by pH and EC meter, respectively (Okaton), while Fe, NO_3 and SO_4 were quantified in the field by Hanna field kits (Table 2.1).

Table 2.1: **Field measurement of some chemical properties of irrigation water**

S. No	Parameter	Kit/Instrument	Procedure
1	pH/EC	Oakton® pH meter (Vista, CA, USA)	10 ml water was taken from the running pump and pH/EC electrode was dipped for 3 min.
2	Arsenic (As)	Econo-Quick (EQ) kit manufactured by Industrial Test Systems Inc.	50 ml irrigation water was taken and added the required reagents and placed it for 12 min. which was later compared with the standard strip of As.
3	Iron (Fe)	Iron HI 3834, HANNA	A colorimetric chemical test kit that uses the phenanthroline method to measure total iron concentration within a 0 to 5 mg/L (ppm) range.
4	Sulphate (SO_4)	Sulphate HI 38000, HANNA	It uses the turbid metric method to determine the sulphate concentration in water samples within a 20 to 100 mg/L range.
5	Nitrate (NO_3)	Nitrate HI 3874, HANNA	A chemical test kit that uses the cadmium reduction method to determine nitrate concentration in samples within a 0 to 50 mg/L range

2.3.2 Laboratory measurements

The water samples were acidified to 1% high-purity HCl (Fisher Scientific Optima) at least one week before analysis by high-resolution ICP-MS on a Thermo-Finnegan Element at Lamont Doherty Earth Observatory (LDEO), Laboratory of Columbia University, New York, USA following the method of Cheng *et al.* (2004). To verify the accuracy and precision of the method, Lamont Doherty Earth Observatory (LDEO) of Columbia University, New York (LDEO) standard (430 μg/L As) and reference materials NIST1640A (8.08±0.07 μg/L As) and NIST1643F (58.98±0.7 μg/L As) were included with every run (Table 2.2).

The soil samples collected in polyethylene bags were sun dried and homogenized. Out of total 660 soil samples, 103 samples were analyzed for As using Innov-X Delta

Premium field X ray fluorescence spectrometer in the soil mode for a total counting time of 90 seconds. The soil standard 2711 obtained from the National Institute of Science and Technology was analyzed at the beginning and end of each day (first day: 102 ± 4 mg/kg at the beginning and 104 ± 4 mg/kg at the end with n=40; and second day: 110 ± 4 mg/kg at the beginning and 104 ± 5 at the end with n=60) and the values were correlated with the reference value of 105 ± 8 mg/kg.

Soil salinity was measured by the method given in USDA Handbook 60 (Richards, 2012) whereby soil EC was measured by extracting the soil samples with water in 1:5 ratio. Soil organic matter was determined by Walkley-Black rapid titration method (Walkley, 1947).The texture was determined by hydrometer method (Ahmad, 1983).

The rice grain samples were milled in coffee grinder and digested with 1% HNO_3 and analyzed by ICP-MS following 50x dilution. Overall, rice grain samples of 60 fields (3 batches from each field) were analyzed for As concentration. For quality control, the same procedure was followed to measure the As content of the standard SRM1568a obtained from the National Institute of Standards and Technology (NIST). The As concentrations measured by analyzing 3 batches of SRM 1568a using the above procedure was 0.28 ± 0.02 mg/kg which were comparable to the certified value of 0.28±0.01 mg/kg.

Speciation for As was done at field by the columns provided by Columbia University and analysed at PINSTECH for speciation. Fe and Mn in soil samples were determined by AAS following standard methods (Farooqi *et al.*, 2007)

Table 2.2: Summary of the As standards run

Standard	As75(hr) (ug/L)	% Error
LDEO2009(1)	409.59	-4.75%
LDEO2009(2)	420.01	-2.32%
LDEO2009(3)	425.13	-1.13%
LDEO2009(4)	404.78	-5.86%
NIST1640A(1)	8.25	2.11%
NIST1640A(2)	7.78	-3.71%
NIST1640A(3)	7.61	-5.70%
NIST1640A (4)	7.74	-4.11%
NIST1643F (1)	60.68	0.38%
NIST1643F (2)	57.85	-4.31%
NIST1643F (3)	55.73	-7.80%
NIST1643F (4)	59.44	-1.66%

Phase 2

In the second phase, sprinkler irrigation system was installed in the fields which were badly affected by As contamination. The objectives of this part of the study are given below:

1. Assessment of sprinkler irrigation on the transfer of As from soil to soil-water and from soil- water to the rice plant and the rice grain in As-affected area.
2. Water conservation by growing rice with sprinkler irrigation instead of the traditional flooding method
3. Assessment of the impact of sprinkler irrigation on the yield of rice

Hypothesis for this research component is that sprinkler irrigation can conserve water in a water-scarce country like Pakistan and could contribute to food security by maintaining yield despite elevated As in soil. Besides, sprinkler irrigation prevents reducing conditions to develop around the roots of the rice plant, in contrast to flood irrigation, resulting in lower arsenic accumulation in rice grains.

2.4 Selection of As Contaminated Soil and Tube Well

On the basis of the previous study carried out by a PhD student, water quality of more than 2000 tube wells along the three floodplains viz. Ravi, Jhelum and Chenab have been tested during field visits. Furthermore, the research also tested paddy soils and rice plants and emphasized on various parameters i.e. arsenic, nitrate, pH, EC, fluoride, iron, and sulfate. The As concentration in the two floodplains, Chenab and Jhelum, was found to be within the permissible range 50 µg/L whereas some areas along the river Ravi tend to have high As concentration, e.g. Khudpur village located near Lahore city on Multan-Ferozpur road. In this village, the tube well which is used to irrigate the crops contained As concentration of 500 µg/L (0.5 mg/L) which is more than the WHO limit of 0.01 mg/L. Because of As contaminated water, soil has also been contaminated by water supplied with As concentration ranging between 30-60 mg/kg. So the rice plant is also at higher risk of As contamination, therefore sprinkler irrigation system was installed in this village to study the effect of this system on As concentration in rice plant.

2.5 Field Site and Sprinkler Installation

A field experiment was conducted with the support of local farmer named Mr. Muhammad Munir in Khudpur village, located near Lahore city on Multan - Ferozpur road. In this region, rice fields have been irrigated with shallow tube well (STW) water during the “Boro” season for 7 to 18 years. Fields are ploughed in the beginning of July and then flooded for 3-5 days before planting of rice in mid of July. Two As contaminated fields having 30-60 mg/kg As concentration were chosen for the rice cultivation. Tube well which was used for the irrigation purposes of both fields was also highly contaminated with As containing 0.5 mg/L. One field was irrigated with traditional method named as flooded field and the other field was irrigated with sprinkler irrigation method named as non-flooded field (Fig. 2.3). Third field which is taken as a control field was irrigated with surface water using traditional method. The area selected to cultivate rice via sprinkler irrigation, traditional method and surface water measured 630 ft^2 each. The data pertaining to the filed site are given in Table 2.3.

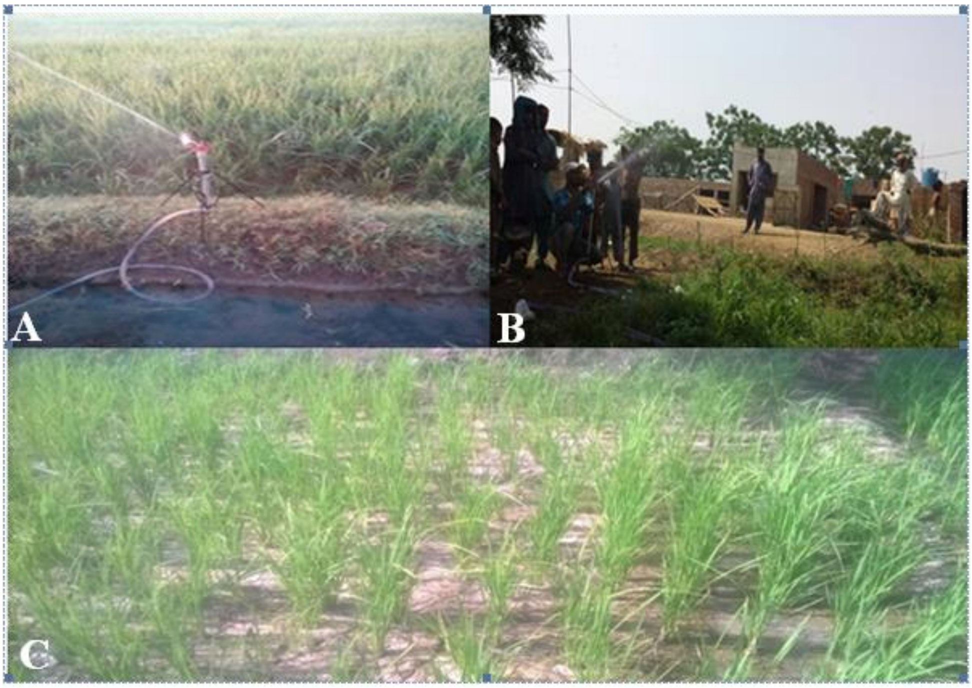


Fig. 2.3: Aerial view of field sites (A, B - Sprinkler Irrigation Technique; C- Rice plant)

Table 2.3: Field site data

Location	Village Khudpur, Okhas Chung, Multan road Lahore
GPS	31°23’40.42”N74° 4’49.63”E
Irrigation History	STW established in 2001
Size of field plot	630 ft^2
Soil texture	Silty clay loam
Flow rate of sprinkler	20 l/min
Flow rate of pump	350 l/m
Running time of sprinkler	40 min/day
Running time of tube well	20 min/week
Total season-long pumping hours	3.5 hr (Note: The area is not flooded so no sedimentation occurs)

2.6 Soil Sampling and Analysis

In June, prior to planting rice, soil samples from all of the three fields were taken from different points. Soil samples which were taken from flooded field points are denoted by T1, T2, T3 and T4. Similarly soil samples which were taken from non-flooded field points are denoted by S1, S2, S3 and S4. Samples which were taken from control field points are denoted by C1, C2, C3 and C4 from inlet onwards to outlet. The soil EC/pH was measured by Oakton® pH meter by extracting the soil samples with water in 1:5 ratio. Further, these samples were analyzed by using As kit in the field to determine As content in soils. After transplantation of rice, the same method was applied throughout the season for soil sampling from all three non-flooded, flooded and control fields points. The distance of one sampling point to another in all the three fields was approximately 2 ft. After every two weeks, soil samples were collected in zipper bags from these above mentioned points to analyze the soil properties throughout the season with the help of As kit. Later, these soil samples were brought to Environmental Hydro Geochemistry Lab at Quaid-e-Azam University, Islamabad, Pakistan to analyze the As content in the soil samples through AAS.

2.7 Irrigation

Shallow tube well (STW) was used to irrigate rice (*Oryza sativa* L.) throughout the growing season. The water input through rainfall was very low so it was neglected. Sprinkler was installed on the corner of sprinkler field (Fig. 2.3-A) using the same As contaminated water. Water was sprinkled to the field on daily basis in the beginning of season for 40 minutes. After one month when rice plants started growing, the frequency of sprinkling water was reduced. Sprinkling time of 40 min was kept constant but water was sprinkled after every 15 days to the rice field. On the other hand, flooded field was irrigated through traditional method of applying water to field after every week for twenty minutes whereas; the 3rd field was irrigated with surface water by conventional method. Operation time of irrigation of all fields throughout the season was calculated to evaluate the water input. Rice field pictures are given in Fig. 2.4.

Fig. 2.4: Actual site photos of rice fields

2.8 Plant Sampling

Plant samples included rice roots, stems, leaves and grains which were obtained on the harvesting day. Application of water to the rice plant was ceased 10 days before harvesting, because irrigation would normally stop at this point in the field. After measuring plants' height, rice plants were harvested by cutting the stems 4 cm above the soil. Basal part of the harvested plants was washed in tap water to avoid any contamination followed by the separation roots, stem, leaf and grain from rice plants. Rice grains were separated from their husks using a pestle and mortar. After harvesting the rice plants, the soil was left to dry. Roots were separated from the soil during disaggregation and sieving to less than 2 mm. However, small portion of the roots also was also made to pass through the sieve and it was considered as part of the soil for the purpose of the study. Plant biomass harvested at each sampling point was washed in tap water and dried at 50°C for 48 hrs. Plant samples were harvested at the end of season and collected in zipper bags and brought to the Environmental Hydro Geochemistry Lab, Quaid I Azam University, Islamabad, Pakistan to analyze the As concentration through AAS.

2.9 Samples Processing and Chemical Analysis

Separated parts of rice plant i.e. roots, stems, leaves and grains were oven-dried and ground in a mill to pass through a 2-mm sieve. Oven dried samples were ground separately using a Retsch-grinder. All the dried ground samples were stored in a desiccator until required for chemical analysis. Roots, stem, leaf and grain samples were digested in HNO_3–H_2O_2 to for As analysis. Two gram of oven dried, ground plant material was weighed into a dry clean 75-ml digestion tubes. 25 ml concentrated HNO_3 was added to each of the tubes and allowed to stand overnight. The following day, these tubes were placed on a heating block and incubated at 60°C. After adding six 1-ml aliquots of 30% H_2O_2 to each of the tube, the temperature was gradually raised to 120°C and the samples were allowed to digest in H_2O_2 for 3 h. The digests were then cooled and diluted to 50 ml with deionized water and filtered through Whatman No. 42 filter paper into acid-washed plastic bottles. As concentrations in roots, stems, leaves and grains were then analyzed using a hydride generator AAS Perkin-Elmer 3300.

2.10 As Speciation

The speciation of arsenic was carried out using column speciation method. The method is used only for the removal of inorganic species of arsenic. The adsorbent in the column (cartridge) retains As^{+5} whereas As^{+3} is allowed to pass through in the filtered water (Fig. 2.5). The concentration of As^{+5} in water was determined by the following equation:

As_T = Total As in raw or 0.4 μm filtered water

As^{+3} concentration = Total As in column filtered water

As^{+5} concentration = As_T - As^{+3}

2.11 Water Calculations

The total depth of water applied for entire season was calculated using the formula;

QT= AD

D= QT/A

Q= Discharge, T= Time of irrigation

A= Area (Farm size), D= Depth of Water

The total groundwater pumped in a sample field was estimated by recording the daily operational hours of every tube well (T) and of sprinkler. The discharge (D) of the tube well was measured by volumetric method using a bucket of known volume (20 l) whereas the sprinkler discharge was known to be 20 l/m.

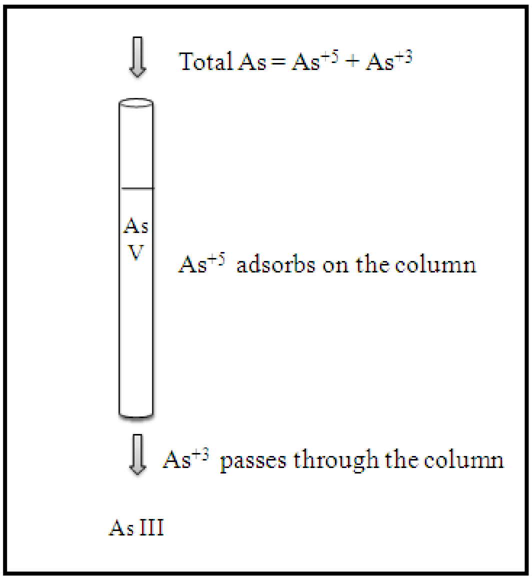


Fig. 2.5: On-site column speciation method for inorganic arsenic species

2.12 Yield Calculations

Rice yield was calculated from two fields;

- Fields irrigated with traditional flooding method with As >100 µg/L,
- Fields irrigated with sprinkler method with As >100 µg/L

For measurement, ten mini samples of 1m^2 each were harvested and rice grain yield was recorded by weighing the grain obtained from 1m^2 and then average yield per m^2 was calculated usind the average yield per m^2, rice grain yield was calculated for plot area of 58.54 m^2 and also in kg/ha.

3. RESULTS AND DISCUSSION

3.1 Spatial Variability of As in Irrigation Water and Paddy Soils

The average concentration of As in irrigation water samples obtained from different districts was found in the following order: Narowal > Lahore > Gujranwala > Gujrat > Mandi Bahauddin > Sialkot, respective concentrations being 76, 54, 10, 8.7, 3.4 and 3.0 µg/L (Table 3.1). The results showed that only 1% samples were above the FAO limit (0.1 mg/L As) for irrigation water. These 1% samples belonged to the Narowal and Lahore districts while none of the samples exceeded the FAO limits in the other four districts. However, 56% samples were above the WHO limit of 0.01 mg/L for drinking water.

Table 3.1: Concentration of total As (µg/L) in irrigation water in different districts of Punjab

District	n	Minimum As (µg/L)	Maximum As (µg/L)	Mean As (µg/L)	Std. Deviation As (µg/L)
Narowal	10	43	102	76	16
Lahore	10	7.26	135	54	37
Gujrat	10	0.54	21	8.7	7.6
Gujranwala	10	0.3	27	10	8.9
Mandi Bahauddin	10	0.23	13	3.4	4.6
Sialkot	10	0.2	6.8	3.0	2.0

Further, the data showed a similar trend of As concentration in irrigation water and paddy soil samples taken from the six districts i.e. the areas where the concentration of As in irrigation water was high, it also showed the elevated concentration of As in paddy soil (Table 3.2).

Table 3.2: Total As in paddy soils (mg/kg) in different districts of Punjab

Districts	n	Minimum As (mg/kg)	Maximum As (mg/kg)	Mean As (mg/kg)	Std. Deviation As (mg/kg)
Narowal	100	3.1	90.10	13.42	15.63
Lahore	100	3.1	55	14.72	12.66
Gujrat	100	3.1	36.83	4.88	3.77
Gujranwala	100	3.1	36.83	4.04	3.97
Mandi Bahauddin	100	3.1	36.83	4.49	3.91
Sialkot	100	3.1	3.1	3.09	4.44

The data in Fig. 3.1 shows the geographic variation of As in all the three flood plains and the two doabs. Ravi flood plain had a higher As concentration in irrigation wells than those from the Chenab and Jhelum flood plains. In Jhelum and Chenab flood plains, none of the wells were found to have As concentration greater than 50 µg/L whereas in Ravi flood plain, 65% of the wells exceeded 50 µg/L and 10% exceeded 100 µg/L. On the other hand, Rachna doab was found to have higher As concentration compared to Chaj doab which lies between Chenab and Jhelum rivers but overall As concentration was lower than all the floodplains. This difference between the floodplains and doabs clearly shows that wells with higher concentrations of As are concentrated near the river bank. Furthermore the results of irrigation wells indicate a clear trend of decreasing As concentration from Ravi to Jhelum flood plain i.e. from east to west. A recent study by Rabbani *et al.* (2017) showed similar trend of decreasing As concentration while moving away from River Indus bank in district Khairpur, Sindh, Pakistan. The reason for this may be the riverine recharge flows due to over pumping as suggested by Berg *et al.* (2007), Hoque *et al.* (2007) and Stahl *et al.* (2016) for the south Asian aquifers. In this study we also speculate that river water is recharging the aquifer in areas around Ravi, and that it is becoming high in As where it flows through the recently deposited river sediments; however this requires further research. The observation regarding the difference of As concentration of irrigation wells in three flood plains and two doabs is very much consistent with the published work of van Geen *et al.* (2017)

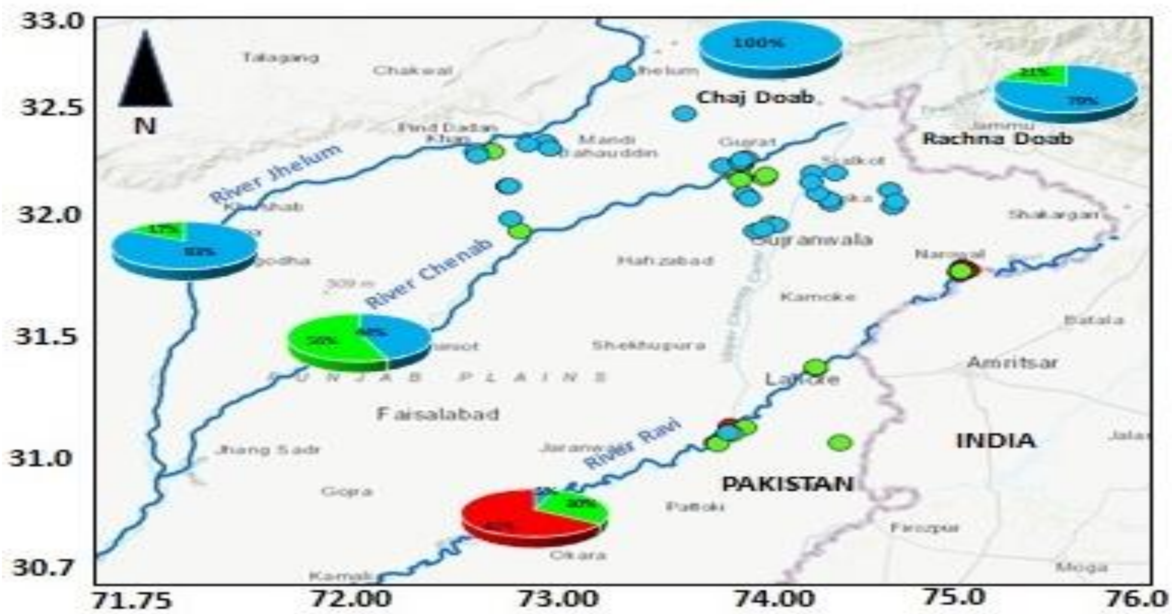


Fig. 3.1: Map showing the concentration of As in three flood plains (Ravi, Chenab and Jhelum) and two doabs (Chaj and Rachna). Blue color indicates As concentration from 0-10 µg/L, green color 10-50 µg/L and red color stands for >50 µg/L

on drinking water that demonstrated that villages within the floodplain of the Ravi River are consistently associated with an elevated proportion of high-arsenic wells. Similar observations were also reported for groundwater As concentrations across the different geo-morphological units of Bangladesh (Ravenscroft, 2001). Various factors control the variability of As level in groundwater, and these include: sediment geochemistry, recharge potential, thickness of surface aquitard, local flow dynamics and degree of reducing properties of aquifers (Sharif *et al.*, 2008). However, this study does not explore the factors that contribute to geographic variation in irrigation well water; it rather questions whether As content of paddy soil relates to irrigation water.

3.2 Use of Field Method to Assess Total As in Rice Soils

The concentration of total As in rice soils measured by X-ray fluorescence (XRF) ranged from 2.7 to 123 mg/kg, out of which 81 samples (79%) were less than 15 mg/kg; whereas soil As determined by EQ Kit ranged from 1 to 50 mg/kg, out of which 92 soil samples (89%) were less than 15 mg/kg. To understand what the arsenic EQ Kit measures when used on soil, we compared soil As measurements made with the field kit to total As as measured by XRF spectrometer on selected 103 soil samples and found a good correlation between total soil As and kit As measurements (R^2= 0.656) (Fig. 3.2). Out of 92 soil samples with As value < 15 mg/kg, the EQ Kit results were consistent with XRF analysis for 81 samples (88%) whereas EQ Kit underestimated

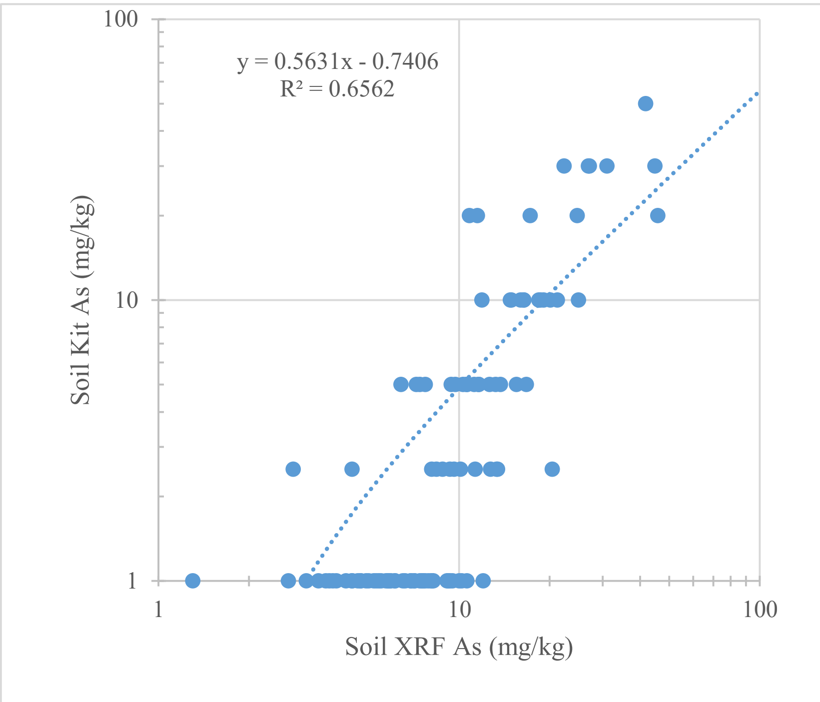


Fig. 3.2: Correlation of total soil As determined by field kit v/s XRF method on log scale (n=103).

As content of soil to be less than 15 mg/kg in 11 soil samples (12%) which actually were greater than 15 mg/kg in the 92 soil samples (Table 3.3). The remaining 11 samples (out of 103 samples) were correctly identified by the Kit to be greater than 15 mg/kg. One of the major misclassifications by EQ Kit was related to underestimation of As for one soil sample which contained 123 mg/kg As by XRF and the EQ Kit reading was 50 mg/kg for that sample.

Table 3.3 Comparison of field kit results for As with XRF measurements with reference to 0-15 mg/kg (n=92), the kit readings for 81 samples (88%) were confirmed by laboratory measurements whereas 11 (12%) samples were misclassified (i.e. underestimated).

Kit As with number of samples		
XRF As	< 15 mg/kg	81
	> 15 mg/kg	11

Our comparison shows that EQ Kit performs well in the critical range of 0-15 mg/kg soil's total As. One of the possible short comings of EQ Kit is the reference chart provided with the EQ Kit which displays the yellow to brown range of colors expected for soil As concentrations of 0, 1, 2.5, 5, 10, 20, 30, 50 and 100 mg/kg after incorporating the dilution factor based on 50 ml of DI water in 0.5 g soil. Therefore, there are chances that soil samples of which As content is slightly above the 15 mg/kg might be underestimated by EQ Kit but only in those rice fields whose soil As content is slightly higher than 15 mg/kg. Although, the kit measurements are binned to a set of only nine values by visually matching the test strip to a color chart, a positive correlation (R^2= 0.656) shows that field kit is consistent in measuring soil As. This comparison of field kit data with XRF provides a sound basis for screening of soil As. And the results indicate that sending every soil sample to a central laboratory for testing should not be a high priority because of the complex logistics involved in shipping samples. The field kit is convenient in many ways for the on-site measurements of As; the procedure is very simple and even uneducated farmers can easily be trained in testing/screening their soils and secondly it is very cheap (0.3 US $ per test). Therefore, this is most convenient, economical and accessible method in terms of methodology in the developing countries like Pakistan which lack lab/financial resources. The single precaution for the kit is to perform the test in the open air so that the fumes generated can exhaust easily, therefore, this kit is well suited to conduct measurements in open agricultural fields.

3.3 Lateral and Vertical Heterogeneity of Soil As

The Figures 3.3, 3.4 and 3.5 show the soil As concentration in Ravi, Chenab and Jhelum flood plains, respectively. Due to lack of a regulatory standard for As concentration in agricultural soils of Pakistan, we used Japanese threshold level of 15 mg/kg (MOE, 2016). The estimated upper-baseline As concentration for this study area has the threshold value for a “contaminated” site, below which yield reduction should be less than 10% (Duxbury *et al.*, 2009). In Ravi flood plain, 59 out of 200 (about 30%) samples exceeded 15 mg/kg whereas in Chenab and Jhelum flood plains, only 4% and 1.5%, respectively, reached the threshold level of 15 mg/kg. Results clearly indicate that the As concentration of Ravi flood plain soils was significantly higher than those of Chenab and Jhelum. In both Doabs (Chaj and Rachna), the As concentration was low and none of the samples exceeded 3.1 mg/kg. The field data clearly reveals that in individual fields, the soil As contents decreased with the increasing distance from the water inlet, leading to highly variable topsoil As contents with high As concentration near the well (Fig. 3.3, 3.4 and 3.5). This decreasing trend of As from inlet to end of the field is observed in all rice fields of three flood plains except in one field of Chenab

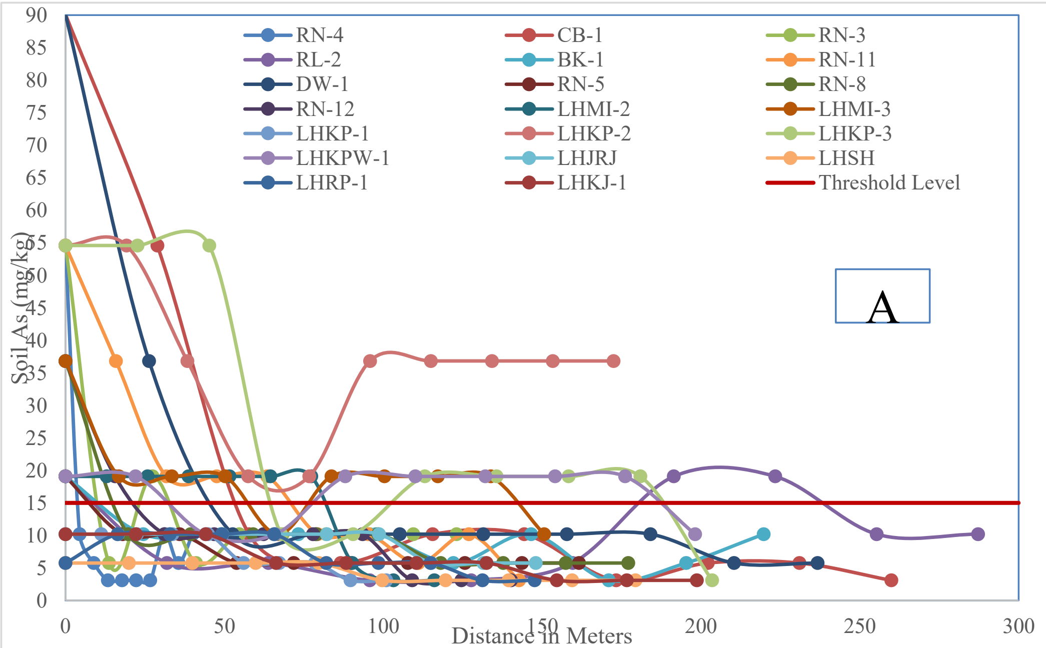


Fig. 3.3: Soil As along a diagonal from source to the end of the field in Ravi Flood Plain (n=200)

where soil As is high at 7th and 9th sample which may be due to the shifting of old well (Fig. 3.4).

Each colored line (Fig. 3.3, 3.4 and 3.5) indicates a specific rice field and the points on the line show the concentrations for every single sample. The distance between sampling points in each field is measured by the equal number of steps. The length of diagonal is measured by Pythagoras theorem after calculating the length and width of each rice field. The red linear line indicates the value of 15 mg/kg i.e. maximum

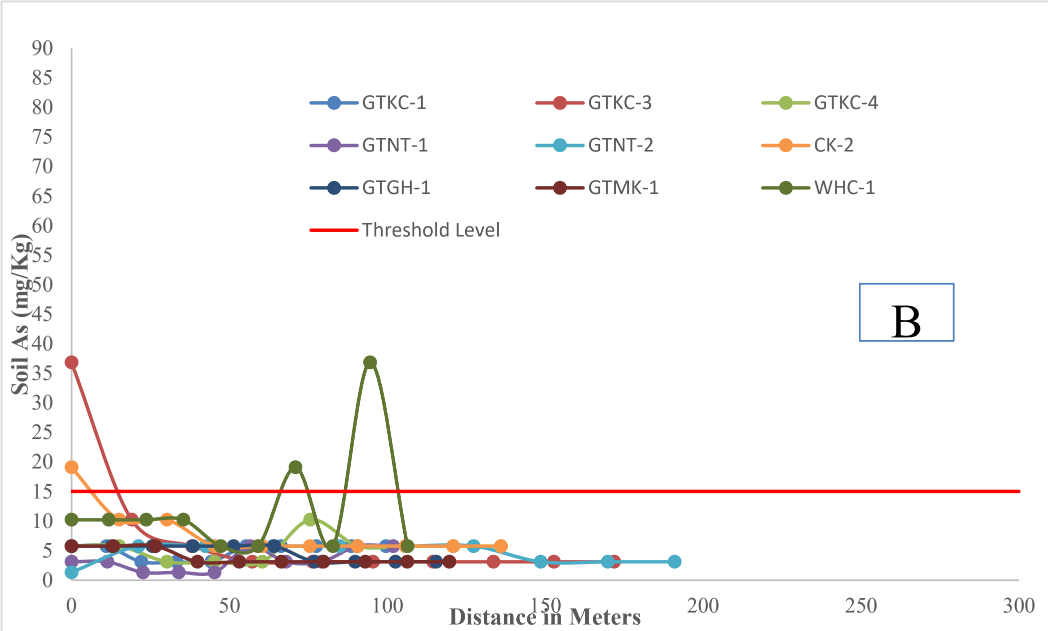


Fig. 3.4: Soil As along a diagonal from source to the end of the field in Chenab Flood Plain (n=90)

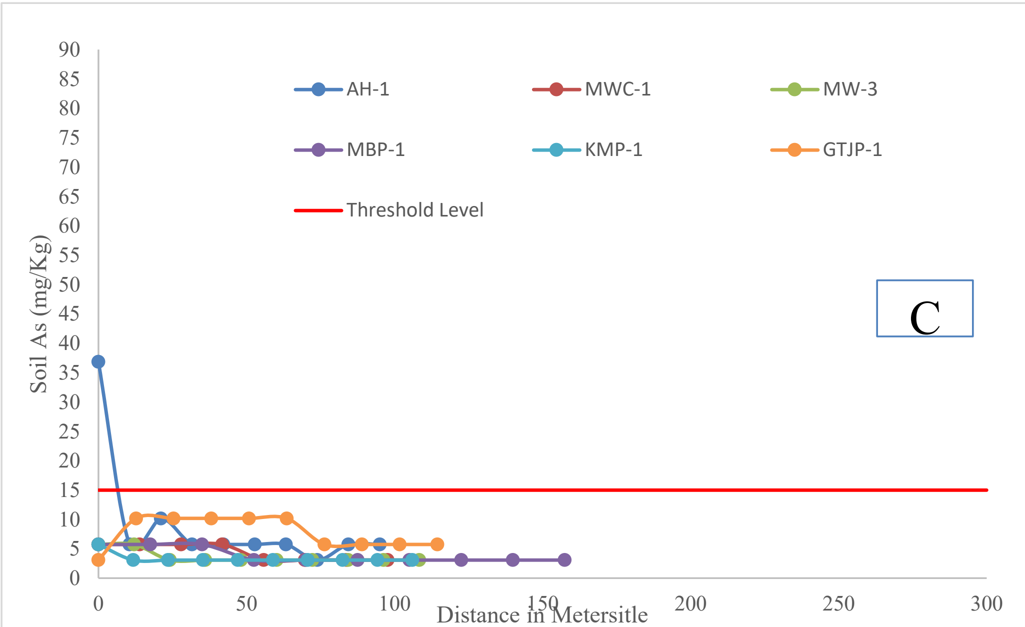


Fig. 3.5 Soil As along a diagonal from source to the end of the field in Jhelum Flood Plain (n=60).

acceptable levels of As in Japanese rice soils (Kitagishi and Yamane, 1981; (MOE, 2016)**.** The soil As concentration was measured by ITS Econo-Quick field kit and converted to equivalent readings by XRF.

To characterize the vertical As distribution, we sampled soil profiles with 10 cm depth intervals up to 60 cm, close to the inlet of ten selected fields of Ravi flood plain (Figure 3.6). Results clearly indicate that soil As is decreasing with depth with higher As

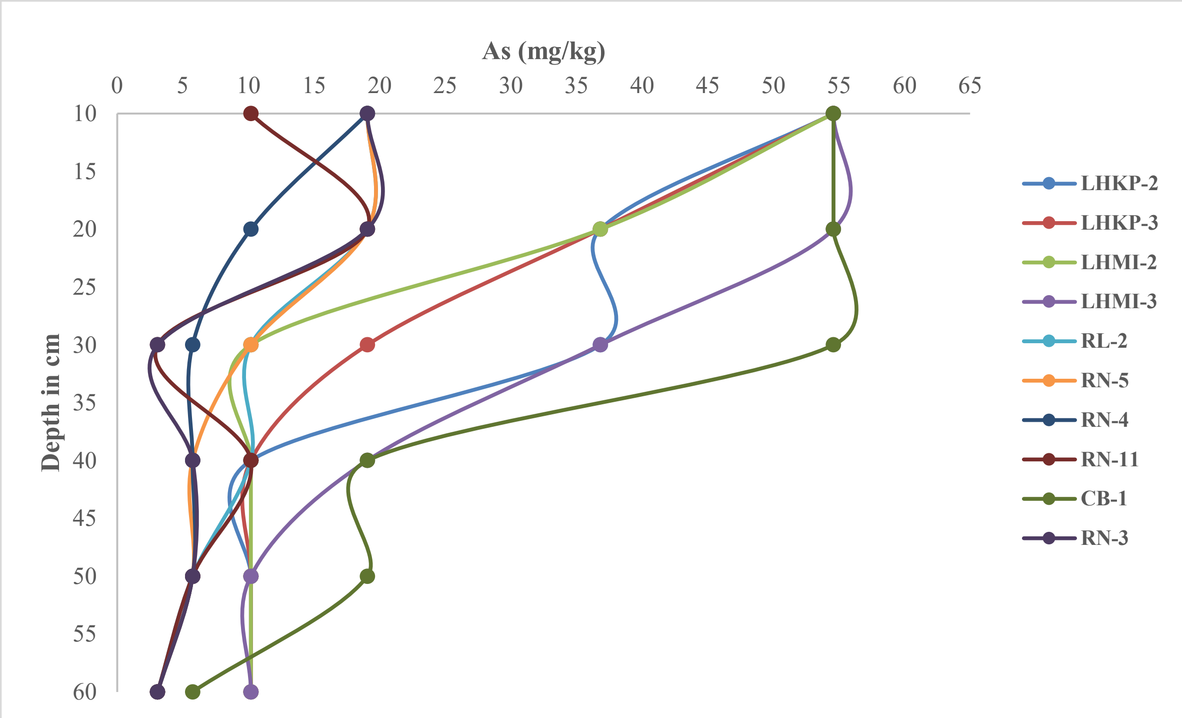


Fig. 3.6: **Soil As in the profiles close to the inlet of ten selected fields in Ravi flood plain.**

content in top soil and low at lower depth (60 cm). At depths below 30 cm, soil As concentrations in all fields were relatively low showing that As input via irrigation is mostly restricted to the soil layers above the plow pan.

3.4 As Speciation

Figure 3.7 depicts the As concentration in the soil samples obtained from the various regions. As^{5+} is exhibited by red color, while As^{3+} is exhibited by blue color on the vertical bars. As^{5+} is dominant to As^{3+} in the soil samples collected from Ravi flood plain near Lahore (LHKP-2, LHKP-3, LHMI-2 and LHMI-3) which means that the oxidized condition is highly prevailing in these areas. Whereas; As^{3+} is dominant to As^{5+} in the soil samples collected from Ravi flood plain near Narowal area (RL-2, RN-5, RN-4, RN-11, CB-1 and RN-3) which means that the soil is highly reduced which favors the release of As^{3+} in soil solution. Total As concentration in soil is the sum of As^{3+} and As^{5+} concentrations.

3.5 Impact of As Rich Water on Accumulation of As in Soil

To further explore as to how much As is actually added to soil by the well, the calculations for each agricultural field are based on paddy soil bulk density of 2500 kg/m^3 and porosity 20% (Meharg and Rahman, 2003). Rice cultivation requires 1-1.6 m of water over the growth season (Huq *et al.*, 2003; Meharg and Rahman, 2003; Erenstein,

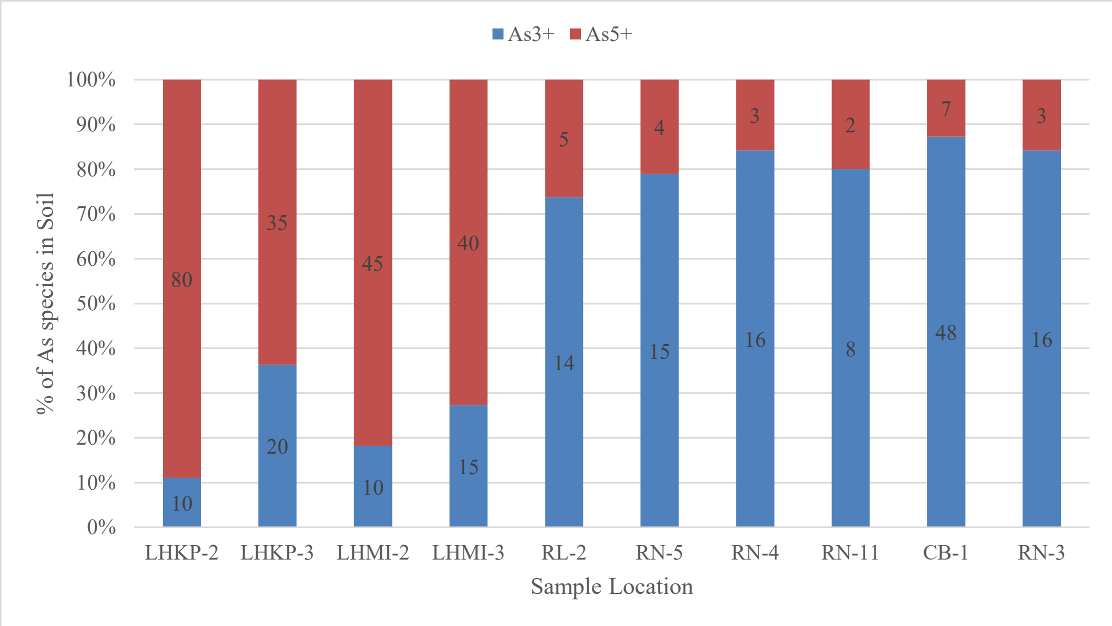


Fig. 3.7: Soil As speciation of the samples close to the inlet of ten selected fields in Ravi flood plain

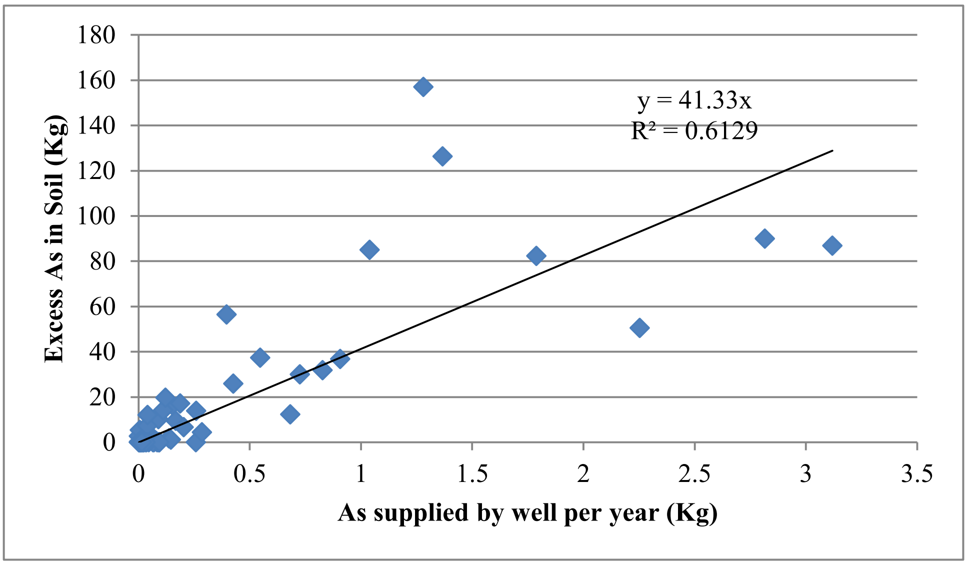


Fig. 3.8: Excess As in soil is plotted against As supplied by well per year (weighted mean As of field) collected at 60 cm depth and at the end of the field by taking the background concentration of 3.1 mg/kg.

2010). Therefore, As supplied by each well in kg/year was calculated by assuming that rice has been irrigated with 1 m of water for growth period and that As is retained in top 20 cm of soil (depth of plough pan). The strong correlation (R^2= 0.613) between As supplied by well and As retained in soil shows the clear input of As by irrigation well (Fig. 3.8). The slope of Fig. 3.8 represents the average well age, so it is evident that these wells are in operation for last 41 years. In this study, since the As concentration varies laterally (high soil As near the inlet and low at the end of the field), therefore, weighted mean of soil As was calculated for each field. Weight was assigned on the basis of the area covered by each sample in 100×100 m^2 field, which is the average size of the field in our study area. In our data, on an average a well with 100 μg/L As supplies 2.81 kg of As per year to the field of 3100 m^2. Assuming that the well is in operation for last 41 years, it is estimated that with unchanged irrigation practice for more than 20 years (irrigation with 100 μg/L of As), the mean As concentration is likely to cross threshold level of 15 mg/kg. Although near the well, the soil As concentrations already crossed the threshold level (Fig. 3.3, 3.4, 3.5).

In case of As in paddy soils there is also a clear west/east divide with much higher concentrations in the east (Ravi flood plain) and this pattern of paddy soil As concentrations relates well to groundwater measurements. A very similar observation was made in a recent study by Chowdhury *et al.* (2017) about different flood plains of Bangladesh. The level of soil As contamination in Ravi flood plain is likely to be toxic to a number of the rice varieties (Duxbury *et al.*, 2009; Panaullah *et al.*, 2009). The results of decreasing As from inlet to end of the field and from top to down in the study could be due to formation and settling of As bearing hydrous ferric oxide (HFO) colloids. Similar pattern of As contamination was also reported in the previous studies conducted in Bangladesh (Dittmar *et al.*, 2007; Roberts *et al.*, 2007).

In this study, the values of excess As above the background status (3 mg/kg) clearly reflect irrigation water input. As discussed, the As content of soil considerably varied within fields with an assumed supply of 1m of irrigation water for last 41 years, therefore, the As content of paddy soil not only depends upon the well's concentration of As but also on the size of a field irrigated by each well and the period for which the field is irrigated with that water. The longer fields of rice are highly variable in As contents due to As bearing HFO aggregates settling during initial water flow as compared to small fields. In this study, the size range of area irrigated by single well ranges from 768 m^2 to 40,363 m^2 indicating that most rice fields are probably not large enough for As bearing HFO settling and seem to be more vulnerable to As contamination. A simple mass balance calculation shows that 976 kg of As has been added to the area of 25,652 m^2 by irrigation wells in Ravi flood plain, which is the most contaminated site. Therefore, with unchanged irrigation practice for decade or two could lead to significant As enrichment as observed in the Ravi flood plain and elsewhere in Bangladesh (Ali *et al.*, 2003; Meharg and Rahman, 2003; van Geen *et al.*, 2006; Saha and Ali, 2007). Furthermore, in Pakistan rice is grown only in summer season with intense monsoon flooding which may result in 13-40% As loss from soil (Huhmann *et al.*, 2017). Thus, apart from areas irrigated with groundwater containing extremely high As levels, areas with high irrigation intensity and limited monsoon flooding may be at particular risk of substantial As accumulation in paddy soils. However, detailed study should be conducted to identify such areas which have limited monsoon flooding.

3.6 Rice Grain As Concentration

The distribution of As in rice grain shows the variations among all the flood plains and doabs (Fig 3.9). In Ravi flood plain, the mean As concentration in the rice grain ranges from 35 to 268 μg/kg, whereas in Chenab flood plain, it ranges from 43 to 218 μg/kg. In Jhelum flood plain, it was the lowest among the flood plains and ranged from 30 to 108 μg/kg. In Rachna doab concentration of As in rice ranges from 57 to 188 μg/kg whereas in Chaj doab, it ranges from 26 to 101 μg/kg. No relationship between rice grain As concentration and total As in soil was found (Fig. 3.10). Unlike water and soil As data which clearly shows that Ravi is different from the other flood plains and doabs, no significant difference was found between flood plains and doabs in case of As in rice grain. Furthermore, both the Rachna and Chaj doabs had higher grain As concentrations despite lower As concentrations in soils and irrigation waters. Within individual fields, there is also variation in the concentration of As with some fields showing large variations compared to the others. The overall average of total As in rice is 0.09 mg/kg which is well below WHO limit of 0.2 mg/kg for rice grain As. It reveals that eating rice does not possess a significant health risks to the population of study area.

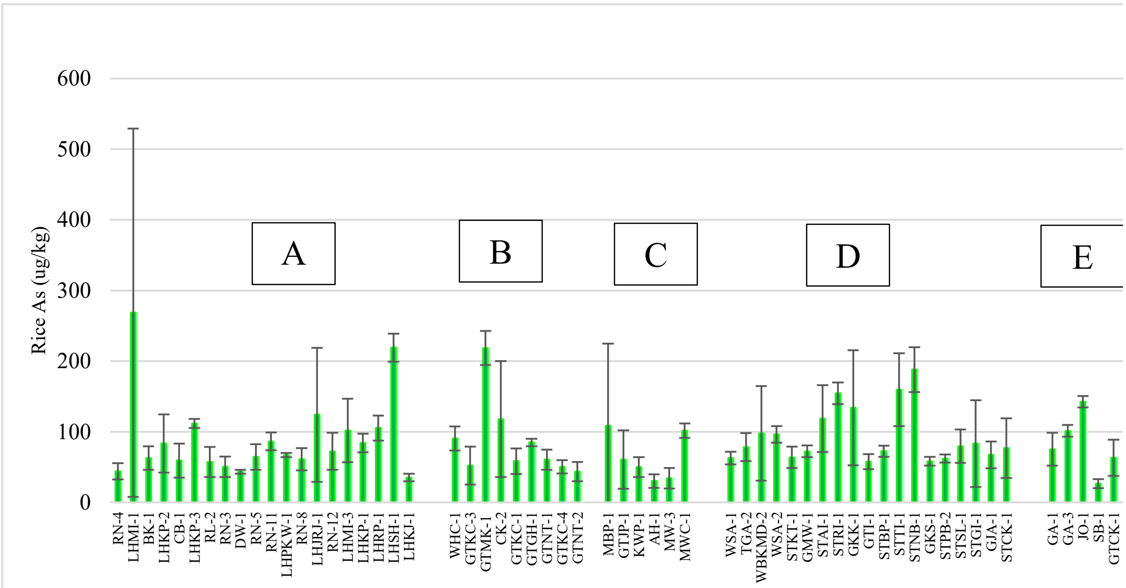


Fig. 3.9: Distribution of As in rice grain: (A) Ravi Flood Plain (n=20) (B) Chenab Flood Plain (n=9), (C) Jhelum Flood Plain (n=6), (D) Rachna Doab (n=19) and (E) Chaj Doab (n=6).

There was a large geographic variation in the grain As concentration between the flood plains and doabs and this variation could not be explained by the variation in soil As concentration. Some of the highest grain As concentrations were detected at Rachna and Chaj doabs despite the sites having low As values in both the soil and the irrigation water. The results are consistent with previous studies which also showed negative relationship of the rice grain's As with that of water/soil As contents ((Islam *et al.*, 2004; Patel *et al.*, 2005; Williams *et al.*, 2007; Duxbury and Panaullah, 2007;

Panaullah *et al.*, 2009; Adamako *et al.*, 2009; Bhattacharya *et al.*, 2010). There are also variations among the different batches of rice obtained from the same field. Similar results were also reported by Stroud *et al.* (2012) who found 2 to 7 fold variations in the concentration of As in rice within individual rice fields; however, no relationship

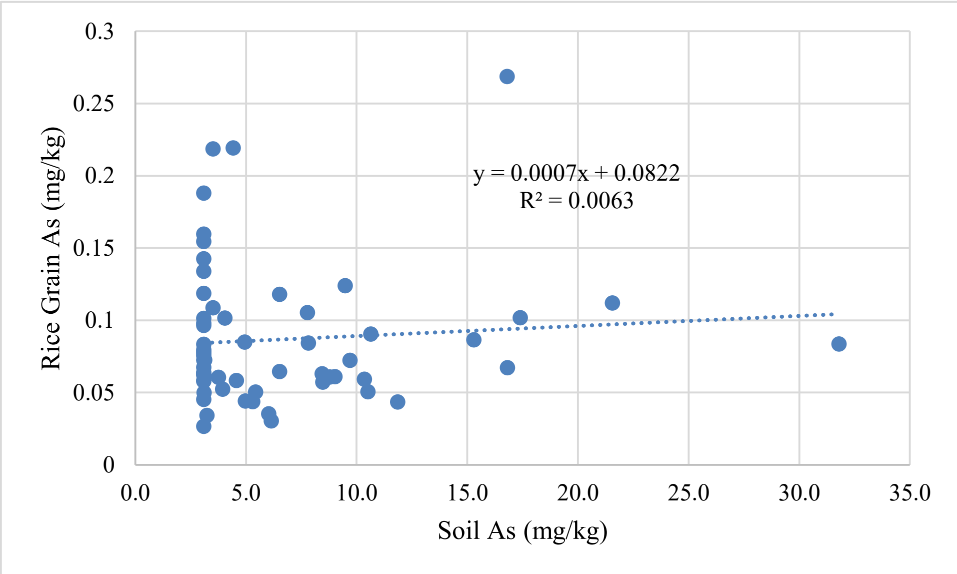


Fig. 3.10: Relationship between soil and rice grain As contents

between grain As concentration with the distance from the irrigation inlet was found.

In this study, rice sampling was not done at equal distance from inlet to the end of field as followed for soil sampling; instead the mean value for rice As of 3 batches collected from farmers field was used. Therefore, the relationship of rice As with soil As concentration within individual fields cannot be drawn. But the important point to note here is that the pattern of As accumulation in rice remains low despite high and low As concentrations encountered in soil. While making predictions as stated above, we recognize that there are many factors contributing to the rice grain As content; soil physical and chemical properties, agricultural conditions and rice processing methods, irrigation water management practices, and genetic differences. For instance, Zavala and Duxbury (2008) observed a higher concentration of As for brown rice than white polished rice and this is because of the fact that brown rice still retains its outer layers (pericarp and bran) which are removed in the whitening (milling) process. Therefore, from the perspective of health risks, these results should be carefully interpreted as they do not represent other rice varieties especially brown rice which are also consumed locally by villagers. Well planned comprehensive studies are therefore required to fully characterize the levels of As in other varieties of rice produced in Pakistan. The present results of rice As contents, however, clearly suggest that large population is not at risk from direct consumption of basmati rice while other concerns such as growing rice with As contaminated water can have reduced yields and the direct ingestion of As from soil by children who spend considerable time playing in rice fields cannot be ignored.

3.7 Reasons for Regional Variability of As in Paddy soils

3.7.1 Role of organic matter in As mobilization and fixation in soil

The organic matter (OM) can play significant role in the mobilization of As in paddy soils through the formation of soluble or insoluble complexes (Wang and Mulligan, 2006). In the present study organic matter content of the paddy soil samples showed highest percentage of OM in district Narowal (5.7%) followed by Lahore (4.4%), Mandi Bahauddin (2.9%), Sialkot (2.7%), Gujranwala (2.2%) and Gujrat (1.1%). Fig. 3.11 shows a weak positive correlation (R^2 = 0.38) between soil OM and As contents, on overall basis. However, a highly significant correlation was obtained between soil As

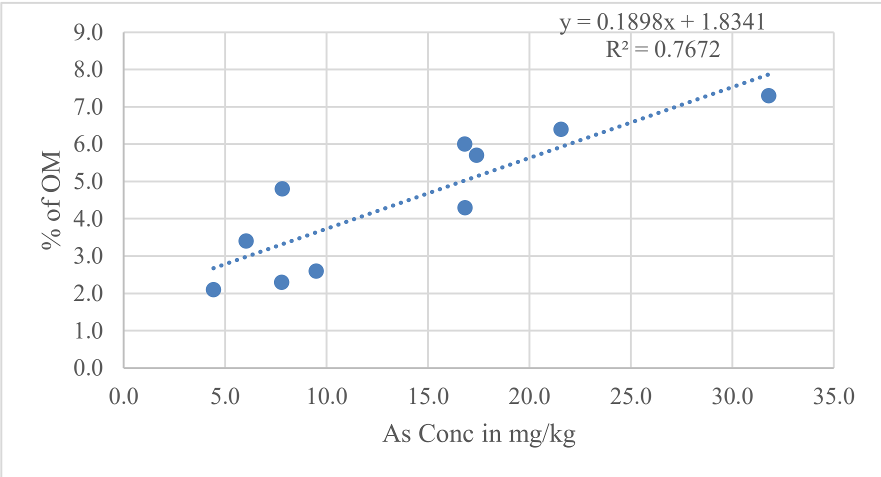


Fig. 3.11: Correlation of OM with soil As.

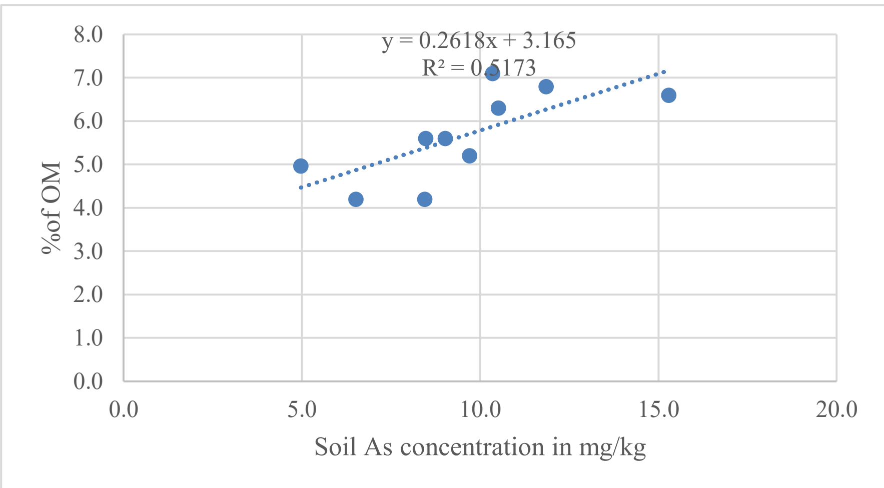


Fig. 3.12: Correlation of OM with soil As in Narowal district

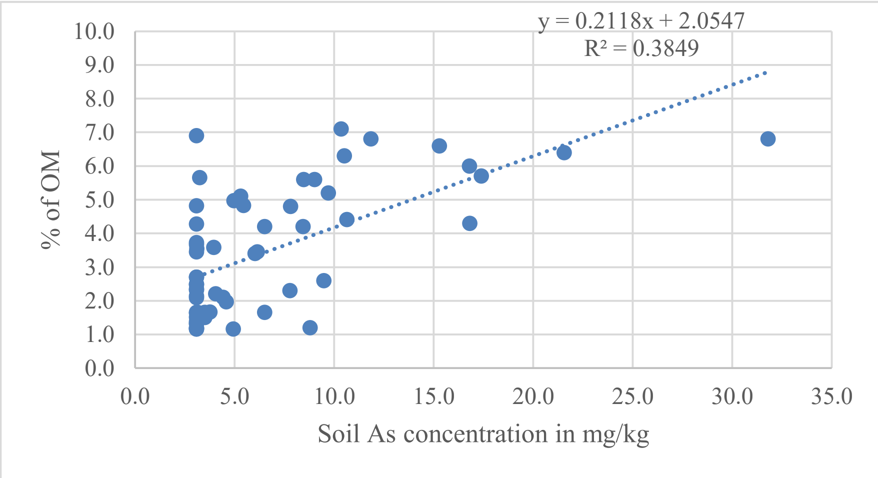


Fig. 3.13: Correlation of OM with soil As in Lahore district

and OM contents in the samples obtained from Narowal (R^2= 0.52) and Lahore (R^2= 0.76) districts (Fig. 3.12 and 3.13). Both of these districts lie in the Ravi flood plain where the concentration of As in irrigation water and paddy soil is also relatively high.

It is inferred from the results that high soil As concentration is associated with the high OM. The study of Smedley and Kinniburgh (2001) also suggested that the elevated concentration of As is associated with high humic acid concentration. Organic matter has a higher affinity for As adsorption, which leads to the formation of an organo-As complex. Therefore, soils containing greater content of OM can decrease As solubility (Lund and Fobian, 1991) due to their higher microbial activity and decreased soil redox potential which favors the reductive dissolution of Fe-oxy-hydroxides . Hundal *et al.* (2013) also suggested that the areas along the alluvial plain contain high organic matter which could have an important effect on the mobilization of As in paddy soil.

3.7.2 Role of Fe and Mn on As availability in soil

The present study showed the total Fe concentration in soil in order of Gujrat > Narowal > Lahore > Mandi Bahauddin > Gujranwala > Sialkot, with average concentration 36011, 29154, 27564, 15589, 24394, and 23943 mg/kg, respectively. Similar results of high Fe, ranging from 12750 to 51750 mg/kg (mean 26960 mg/kg) were also reported by Waseem *et al.* (2014) for the area near Lahore. Overall, 20% soil samples were above the background limit of 29400 mg/kg.

Similarly, total Mn contents of paddy soils were also high. Mean value of Mn (mg/kg) in different districts was: 644 in Narowal, 643 in Lahore, 632 in Gujrat, 566 in Mandi Bahauddin, and 424 in Gujranwala and Sialkot. Ahsan *et al.* (2009) reported Mn content of 553 mg/kg and 449 mg/kg in India while Xie *et al.* (2012) reported it as 386 mg/kg in China. Furthermore, a positive correlation between soil As and Mn was

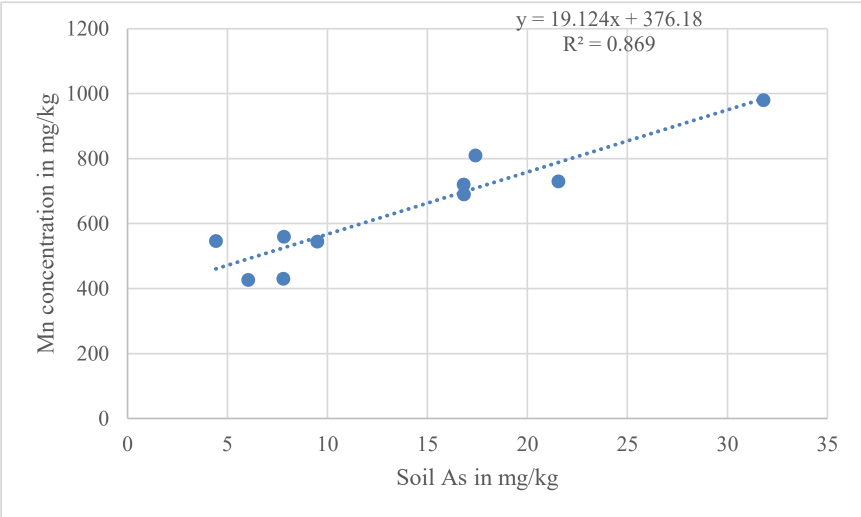


Fig. 3.14: Relationship between soil Mn and As in Lahore district

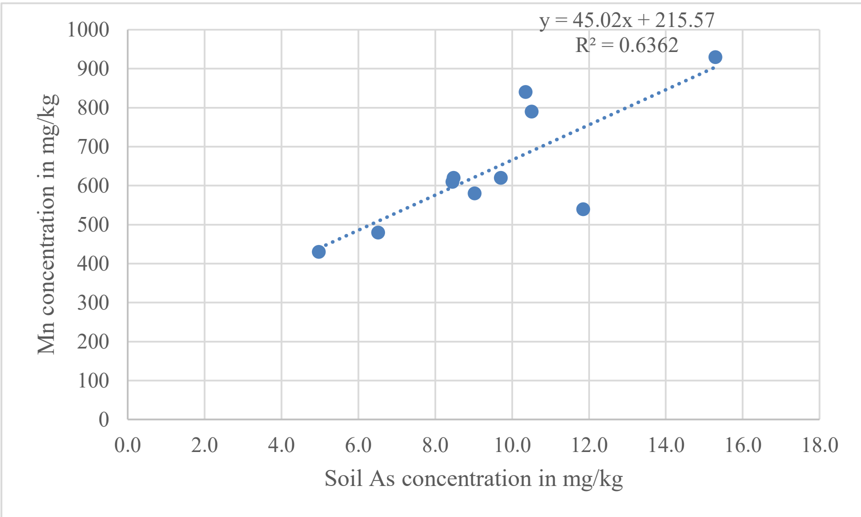


Fig. 3.15: Relationship between soil Mn and As in Narowal district

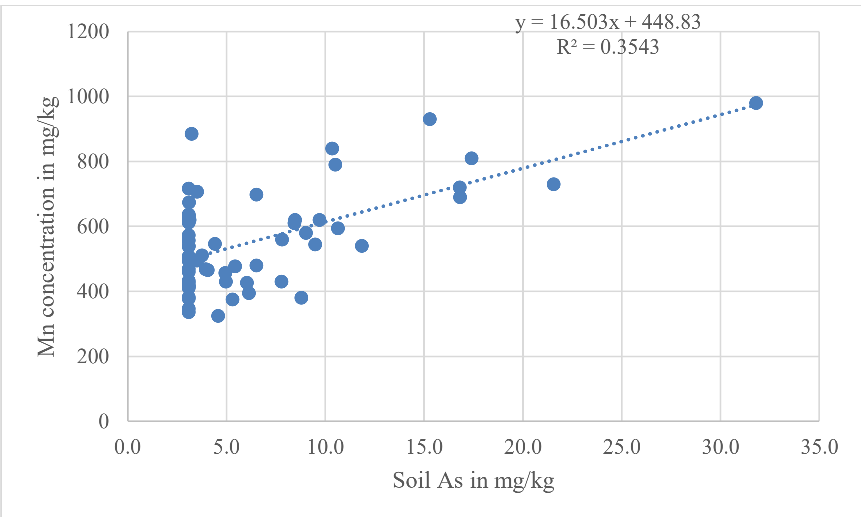


Fig. 3.16: Relationship between soil Mn and As in samples taken from the six districts

observed in Lahore (R^2=0.869) and Narowal district (R^2=0.63). On overall basis, the R^2 value was 0.35 for the correlation between soil As and Mn in paddy soils of the six districts (Fig. 3.14, 3.15 and 3.16). Ahmed *et al.* (2011) also observed a significant positive correlation between As and Mn (R^2=0.86) in Dhamrai soils.

Among these, the samples collected from the Ravi flood plain have significantly high As in water and soil. It indicates that anaerobic soil environment leads to the reducing conditions and subsequently dissolves the Fe-Mn hydroxide that would lead to the leaching of Fe-Mn hydroxide which bounds As into the soil solution (Fu *et al.*, 2011). Similarly, various studies in China, India and Bangladesh also support that reducing condition in paddy soil prevails the mobilization of As in soil (Bogdan and Schenk, 2009). Korte and Fernando (1991) also speculated that desorption of As from Fe oxides can occur in reducing, alluvial sediments and this could lead to high As groundwater.

Furthermore, Fu *et al.* (2011) reported a significant positive relationship between Fe-Mn-bound As and grain As. They observed that under flooded irrigation system, poorly crystalline Fe oxides can readily dissolve as compared to crystalline Fe oxides. The results of this study are in line with the findings by Ahmed *et al.* (2011) who found a significantly positive relationship between As and Fe. The oxy-hydroxide phases of Fe and Mn are commonly found in different soils which are efficient due to their high adsorption capacity. The mobility of As is inhibited by Fe and Mn under aerobic conditions. However, in flooding conditions these phases can enhance the mobility of As (Fitz and Wenzel, 2002).

3.7.3 Role of pH in As mobility

Soil pH can play an important role in the solubility and bioavailability of As, because it controls the As speciation and leachability. Smedley and Kinniburgh (2002) suggested that the development of high pH (>8.5) is one of the important distinct triggers which leads to the solubility of As in irrigation water and soil suspension. The second factor is the presence of reducing condition at near neutral pH. This leads to the desorption of As from mineral oxides and to the reductive dissolution of Fe and Mn oxy-hydroxides. The results of the present study indicated that the pH of paddy soils of Lahore, Narowal, Sialkot, Gujrat, Gujranwala and Mandi Bahauddin were in the range between 8.5-9.4, 8.4-9.4, 8.2-9.3, 8.6-9.3, 8.5-9.2 and 8.7-9.1, respectively. This study showed that there was no obvious relationship between soil pH and As, indicating little or no impact of soil pH on the fixation and mobilization of As in soil. In fact, pH affects the As behavior generally by controlling the interaction between As and its bearing phases, instead of direct action.

A study conducted by Fu *et al.* (2011) also observed that the pH of soil had no significant effect on the accumulation and mobilization of As in paddy soils. However, studies have shown that As^{3+} solubility increases by decreasing the pH within the range, commonly found in soils (pH 3-9). Similarly, Peterson (2005) found that As mobility increases at very low (<5) pH. For instance, at pH 4-9, $HAsO_4$ and H_2AsO^{4-} are common species of arsenate and arsenite which occur as arsenious acid (Sadiq, 1997). While low pH can cause As to be soluble, alkaline pH promotes arsenate (As^{5+}) stability in groundwater. The speciation was not done in the study but in the present study most of the soil pH lies between the ranges 8.2-9.5 so As^{3+} may possibly be a dominant As species in the soil as the paddy soil prevails the mobilization of As under flooded irrigation system (Sadee *et al.*, 2016).

3.8 Variation of As in Individual Fields of Lahore (Sprinkler vs Flood Irrigation Method)

The Fig. 3.17 shows the temporal variation in As concentration in tube well irrigated fields throughout the growing season covering four points named T1, T2, T3 and T4. Concentration of As in soil samples taken at the point T1 is 54.59 mg/kg from 16 July to 29 September, no variation in As content was observed during this period. After that, a sudden increase in As content was observed until the next testing date i.e. 14 October and remained unchanged till the last test (29 October) when the crop was harvested.

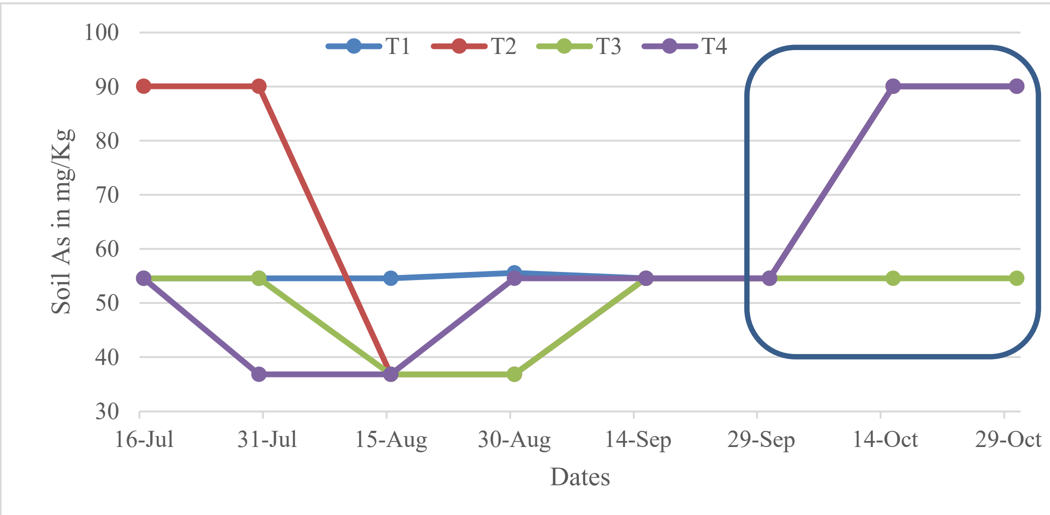


Fig. 3.17: Soil As concentration over the entire growing season in a field irrigated by traditional flooding system. T1, T2, T3 and T4 is the distance from tube well, T1 near to the well whereas T4 is at the furthest distance from the well.

Similarly, the As concentration in soil samples taken at the point T2 is 90.10 mg/kg during the first month of growing season from 16 to 31 July but it decreased to 38.83 mg/kg during the next month from 15 to 30 August. Thereafter, the As concentration showed increase to 54.59 mg/kg from 14 to 29 September and to 90.10 mg/kg from 29 September to 29 October.. At the point T3, the initial As concentration is observed to be 54.59 mg/kg, thereafter a trend almost similar to that of T2 was observed. During the last two months of the growing season from 14 September to 29 October the concentration remained the same as that in July i.e. 54.59 mg/kg. Last sampling point T4, far away from the tube well inlet, showed the initial As concentration as 54.59 mg/kg on 16 July. The next month this concentration decreased to 38.83 mg/kg from 31 July to 15 August, and it again increased to the initial value of 54.59 mg/kg from 30 August to 29 September and to 90.10 mg/kg during the last month from 14 October to the harvesting day on 29 October. Thus, the As concentration in soil at all the sampling points observed throughout the growing season is comparatively higher at the end of the season than at the start of the growing season of paddy rice.

The Fig. 3.18 shows the temporal variations of As in the sprinkler irrigated field monitored throughout the growing rice season at four points viz. S1, S2, S3 and S4. The concentration of As in the soil samples taken at point S1 was 54.59 mg/kg on 16 of July; the very first day. It showed a decline by 33% to 36.83 mg/kg on 30 August and further reduced to 19.01 mg/kg when tested on 14 September and this result remained unchanged until the harvesting day (30 October). Similarly the As concentration in the soil samples taken at point S2 was similar to that recorded at point S1 (54.59 mg/kg) during the first month of the growing season (July); thereafter similar trend of decrease in As concentration (to 36.83 mg/kg) was observed during the next month from 30 July to 15 August. In the following month, the As concentration further reduced to 19.07 mg/kg, and finally to 10.01 mg/kg in the month of harvesting from 14 September to 29 October. At the point S3, the initial As concentration was 36.83 mg/kg as observed on 31 July of the growing season. It decreased to 27 mg/kg when tested on 15 August, and to 19.07 and 10.07 mg/kg on 14 and 29 of October, respectively. Last sampling

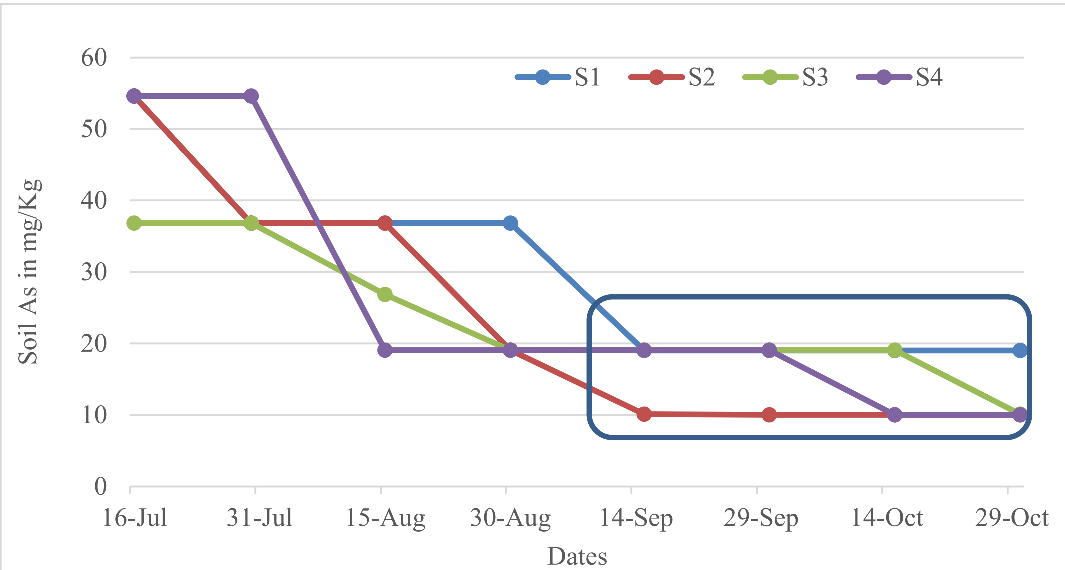


Fig 3.18: Soil As concentration over the entire growing season in the field irrigated by sprinkler system. S1, S2, S3 and S4 is the distance from the source, S1 near to the source whereas S4 is at the farthest end of the field.

point S4 was far away from the sprinkler where the initial As concentration stayed at 54.59 mg/kg from 16 to 31 July. In the following months from mid-August to end of September, it reduced to 19.07 mg/kg; however a further decrease to 10.01 mg/kg was observed during the period from 14 to 29 October.

Natural soils can typically contain 0.1–10 mg/kg of total As (Zhao *et al.*, 2010). The EC recommends that soils should always have As concentration less than 20 mg/kg to be used for agricultural purposes (Shrivastava *et al.*, 2017). FAO recommends the As concentration in irrigation water should be under 0.1 mg/L for agriculture purposes (Buschmann *et al.*, 2007). Different studies have revealed that usage of As-contaminated irrigation water in the concentration range of 100-400 mg/l leads to accumulation of total As in top paddy soil at a rate of 1.0-1.6 mg/kg/yr (Dittmar *et al.*, 2007).

Arsenite (As^{3+}) and arsenate (As^{5+}) are the most commonly found inorganic As species whereas; monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are the frequently reported organic As species in paddy soil-water systems (Honma *et al.*, 2016). Paddy fields which are irrigated with As-contaminated groundwater act as net sinks of As from groundwater and a small amount returns to or replenishes the aquifer (Neumann *et al.*, 2011). These paddy soils and As-contaminated irrigation water are both linked to elevated concentrations of As in the rice grains (Xie and Huang, 1998 ; Heikens *et al.*, 2007). From Fig. 3.17 and 3.18 it can be concluded that the concentration of As in tube well irrigated fields is higher in the last month as compared to the sprinkler irrigated fields.

3.9 Soil As Speciation

The Figures 3.19 and 3.20 show the temporal variations in inorganic As species in soil throughout the growing seasons in both fields i.e. field irrigated by traditional flooding method and field irrigated by sprinkler irrigation system. It is evident that in the field irrigated by the tube well, A^{3+} dominates As^{5+}. With the passage of time the As^{3+} increases by continuous flooding conditions whereas As^{5+} decreases initially and then a rise can easily be observed near the harvesting days. In the sprinkler irrigation, initially As^{3+} and As^{5+} were in almost equal proportions but with the passage of time the As^{5+} dominates As^{3+} due to aerobic conditions and this could be the compelling evidence for low concentration of As in different rice plants. The overall effect is decrease in As mobility and accordingly, less As is available for the plants (Xu *et al.*, 2008). Talukder *et al.* (2011) supports the interpretation that aerobic water regime causes the rice to take up a smaller amount of As (0.23–0.26 ppm) than that under reducing environment (0.60–0.67 ppm). Of the two inorganic forms of As, As^{5+} is the dominant state on the root surface under anaerobic environment of flooded rice field, and it is easily transformed to more mobile water soluble As^{3+}. Therefore, under flooded water condition, As transformation mechanism plays a pivotal role for As concentrations in shoot, leaf and grain (Deng *et al.*, 2010). The status of total root As also depends on oxidizing ability of root (Mei *et al.*, 2009). In addition, this management system affects soil properties with a subsequent harmful impact on the following non-rice upland crops under the prevailing cropping system (Tripathi *et al.*, 2005).

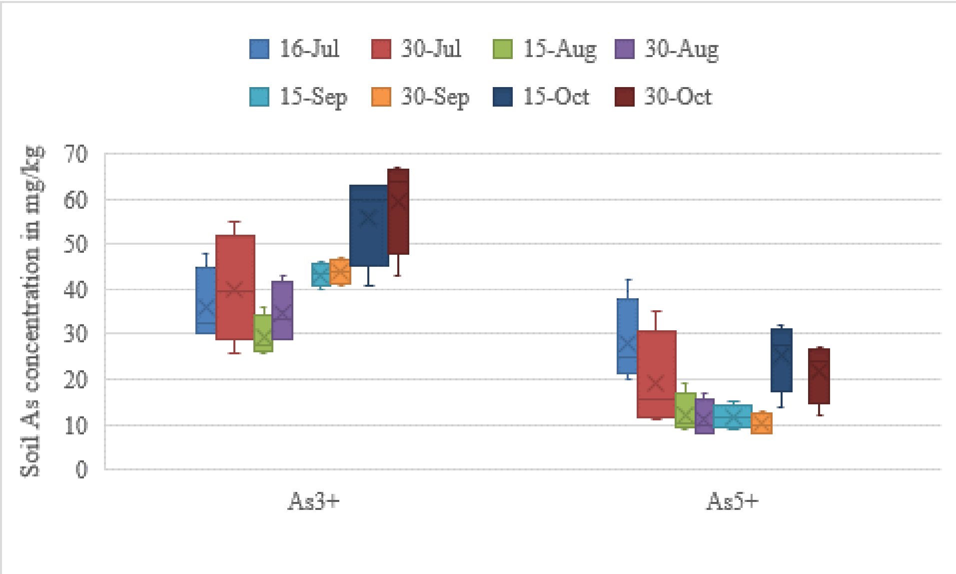


Fig. 3.19: Soil As speciation in the field irrigated by traditional flooding throughout the entire rice growing season

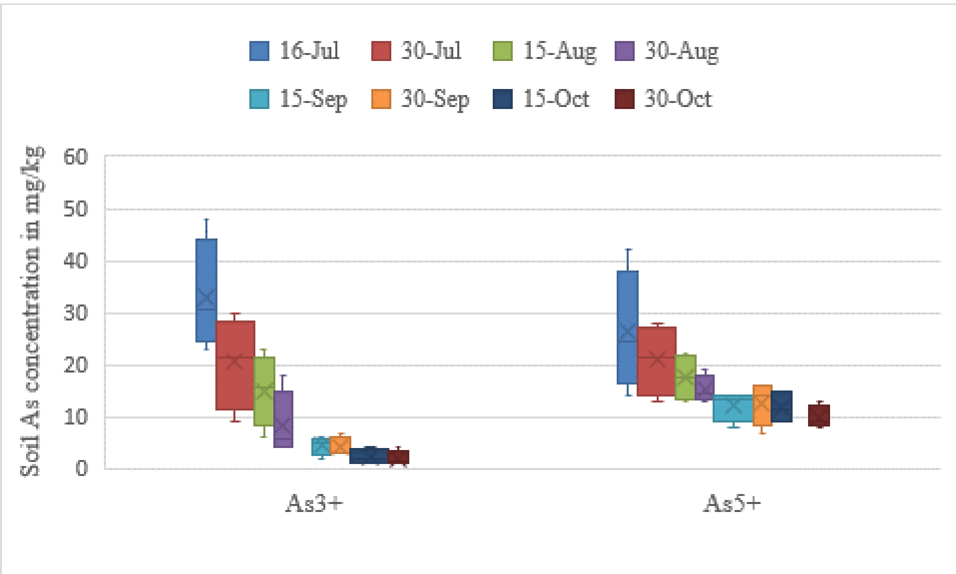


Fig. 3.20: Soil As speciation in the field irrigated by sprinkler method throughout the entire rice growing season

3.10 As Variation in the Different Parts of Rice Plant

The data in Figures 3.21 and 3.22 show that As in the rice grain was generally low as compared to leaf, root and stem. Highest As concentrations were found in root (4.6, 4.2, 3.5, and 3.3 mg/kg), followed by the stem (1.6, 1.3, 1.4, 1.2 mg/kg), leaf (1.5, 1.3, 1.4, 1.2 mg/kg) and rice grain (0.1, 0.1, 0.1, 0.1 mg/kg) in respective plant sampling locations of the field irrigated with traditional flooding. Similar trend was also observed in the field irrigated with sprinkler irrigation system. Under this system, the respective As concentrations in roots were 2.8, 2.6, 2.7, 2.6 mg/kg, followed by stem (1.2, 1.2, 1.2, 1.1 mg/kg). In leaf, the values were nearly the same for the distant plants and the ones grown near to the sprinkler (1.2, 1.1, 1.2, 1.1 mg/kg). The As concentration of the rice grain ranged between 0.07 and 0.06 mg/kg for all plant sampling locations.

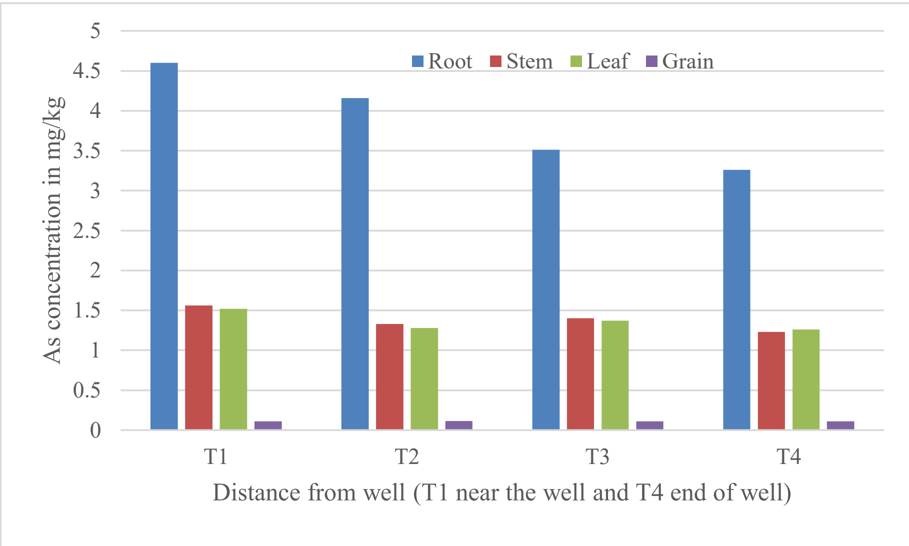


Fig. 3.21: As concentration in different parts of rice plant in the field of Khudpur, Lahore irrigated by traditional flooding method.

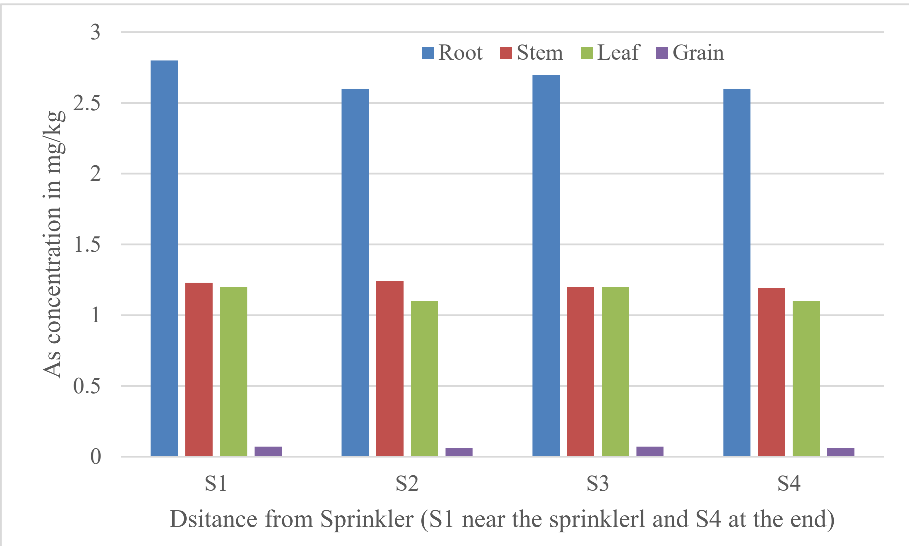


Fig. 3.22: As concentration in different parts of rice plant in the field of Khudpur, Lahore irrigated by sprinkler method

Fig. 3.23 shows the comparison of average As concentration in different plant parts for the two systems i.e. flooded and non-flooded. One of the finding from these results is that the concentration of As in almost all parts of plants decreased in the field irrigated by sprinkler irrigation (31% decrease in roots, 12% in stem, 15% in leaf and about 39% in rice grain) compared to the field irrigated through traditional flooding method. However, plant uptake of As was still observed due to previously accumulated As in the soil through long term use of As contaminated water from the well.

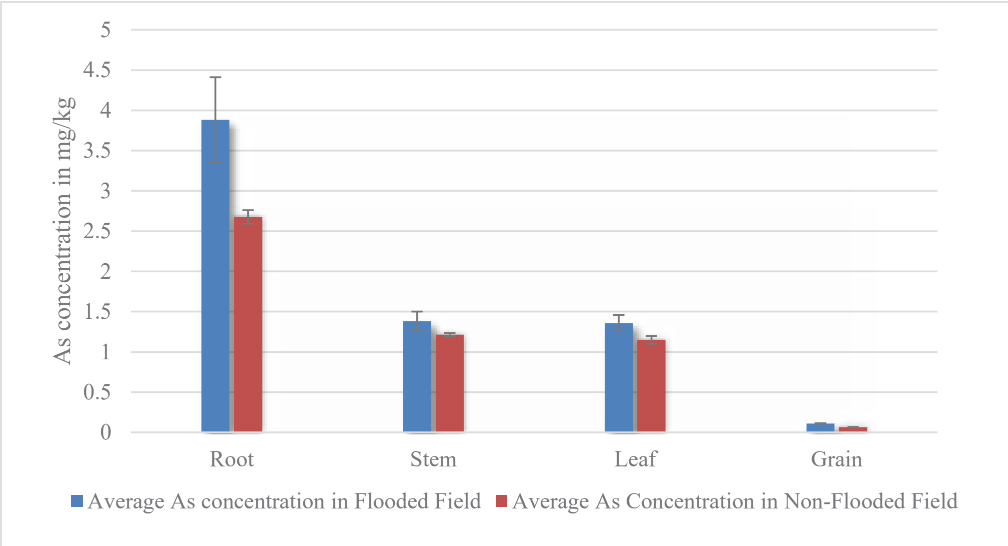


Fig. 3.23: Comparison of As concentration in different plant parts for the two systems i.e. flooded and non-flooded soil

Under aerobic soil conditions, it is anticipated that most of the As content remains bounded to the Fe oxides and is therefore unavailable to plants (Lauren and Duxbury, 2005). Therefore, growing rice under deficit irrigation reduces As loading into the soil-root-shoot-grain continuum (Stroud *et al.*, 2011; Talukder *et al.*, 2011).

Different studies have revealed that usage of As contaminated irrigation water in the concentration range of 100-400 µg/l leads to accumulation of total As in top paddy soil at a rate of 1.0-1.6 mg/kg/yr (Dittmar *et al.*, 2007). Due to the reducing conditions in flooded soils during the rice cultivation season, As availability in the soil solution can further increase with time (Syu *et al.*, 2015). However, contrasting views have also been reported that free Fe oxides in soil or Fe plaques can act as a buffer and enhance the bio available As fraction in soil and the As concentration in rice (Tripathi *et al.*, 2014). Recently, Kramar *et al.* (2017) described that As mainly associated with Fe in rice soil is not equally distributed over a whole soil aggregate but occurs in local enrichments of a few tens of µm in size. However, the investigation of specific As-bearing minerals and their specificity in binding As in soil is still in progress.

The conclusion of this research is supported by three strength points. To begin with, all of the samples were obtained under the same agricultural conditions (geographic location, pedological characteristics and chemical composition of the irrigation water), only variable being the irrigation method used i.e. sprinkler irrigation and continuous flooding irrigation. In addition, the samples were genetically uniform; controlling the variability based on genetic factors and each sample was representative of a specific genotype grown under known conditions. Finally, the analytical methods used to evaluate the As content in the rice and soils were specifically optimized for this study and completely validated, thus excluding a significant bias error from the data.

The Fig. 3.24 shows that the content of As in the rice grain was generally very low as compared to root and shoot and stem. The higher accumulations of As were found in root (1.5, 1.4, 1.2 and 1.1 mg/kg) followed by stem (0.1, 0.1, 0.1, 0.1 mg/kg), leaf (0.07, 0.04, 0.04, 0.03 mg/kg) and rice grain (0.001, 0.001, 0.001, 0.001 mg/kg) for respective sampling locations in a field irrigated with traditional flooding by surface water without As contamination.

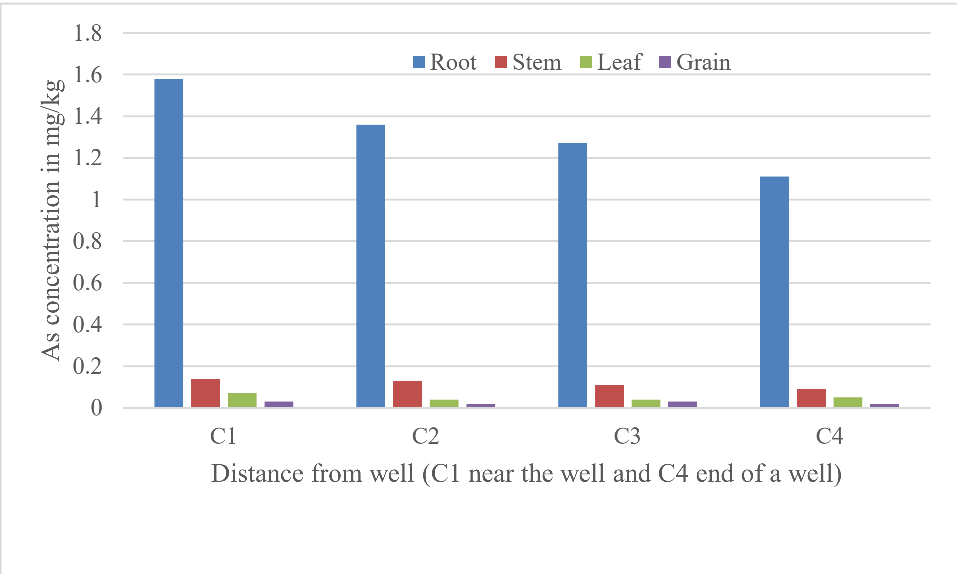


Fig. 3.24: As concentration in control site plants

3.11 Water Conservation through Sprinkler Irrigation Method

Table 3.4 Calculation of the depth of water applied by traditional flooding method

Discharge of the tube well (Q)	300 L/min	0.3 m^3/min	10.6 ft^3/min
Area irrigated by tube well (A)	631 ft^2		
Total time of irrigation for entire growing season (T)	280 min		

The total depth of water applied was calculated using the formula;

QT= AD

D= QT/A

Q = Discharge, T= Time of irrigation

A= Area (Farm size), D= Depth of Water

D = (10.6×280)/631 = 4.70 ft = 1434 mm

Table 3.5: Calculation of the depth of water applied by sprinkler irrigation method

Discharge of the sprinkler (Q)	20 L/min	0.02 m^3/min	0.70 ft^3/min
Area irrigated by tube well (A)	631 ft		
Total time of irrigation for entire growing season (T)	3000 min		

The total depth of water applied will be calculated using the formula

QT= AD

D= QT/A

Q = Discharge, T= Time of irrigation

A= Area (Farm size), D=Depth of Water

D = (0.70×3000)/631 = 3.32 ft= 1015 mm

Water saving in sprinkler irrigation (1015 mm) v/s traditional flooding method (1434 mm) is calculated to be 30%.

Although 90% of worldwide rice production is in Asia, it is also extensively cultivated crop in Africa and America and intensively in some regions of southern Europe, mostly in Mediterranean countries (Hall *et al.*, 2009). With predictions suggesting that many countries will have severe water problems by 2025 (Rosegrant *et al.*, 2002), the continuation of flooded irrigation in rice-growing ecosystems is not desirable due to its lack of sustainability. Therefore, alternatives are required that will allow greater efficiency of water use (Feng *et al.*, 2007). This is especially urgent in the Mediterranean regions and some parts of Asia where the problem of water scarcity is steadily worsening (Sabater and Tockner, 2009). Water has many competing uses, but in the present time the climate change is further aggravating the water scarcity issues by reducing its availability for irrigation purposes (Hafeez *et al.*, 2014). The study by Bouman *et al.* (2007) showed that about 15–20 million ha of irrigated rice is likely to suffer from water scarcity by the year 2025.

Rice yield is mostly dependent on the water type used for irrigation over the respective growth cycle. To prepare the land for rice planting, approximately 150-200 mm of water is added, however, this figure may extend up to 900 mm of water in some instances (Bouman and Tuong, 2001). Throughout the growing season (~3 months), 500 to 3000 mm of water is needed, and this figure differs with climatic conditions, soil type, and rice genotypes (Abedin *et al.*, 2002a; Abedin *et al.*, 2002b).

Rice is traditionally cultivated by conventional agricultural practices involving flooding irrigation, which means high water consumption, large emissions of methane and high global energy costs. In the face of unreliable canal water supplies, many farmers have increased their reliance on private tube wells, placing tremendous pressure on groundwater supplies (Ahmad *et al.*, 2007). Negative environmental effects related to irrigation are increasing as overexploitation of groundwater and poor water management lead to the dropping of water tables in some areas and increased water logging and salinity in others (Qureshi *et al.*, 2003). Agricultural technologies that can reduce production costs, save water and improve production while sustaining environmental quality are therefore becoming increasingly important (Gupta *et al.*, 2002).

Rice is an obvious target for water conservation because it is grown on more than 30% of irrigated land and accounts for 50% of irrigation water (Barker *et al.*, 1999). Rice is an important staple food crop in the world and most widely grown under irrigation with seasonal water needs ranging between 1650 to 3000 mm depending upon soil and climatic conditions (Lampayan and Bouman, 2005; Tuong and Bouman, 2003). In Asia, more than 80% of the developed freshwater resources are used for irrigation purposes and about half of this is used for rice production alone (Dawe, 1998). Until recently, this amount of water has been taken for granted, but now the global "water crisis" threatens the sustainability of irrigated rice production as a result of decreasing water quality (chemical pollution, salinization), decreasing water resources (e.g. falling groundwater tables, silting of reservoirs) and increased competition from other sectors such as urban and industrial users (Belder *et al.*, 2004; Bouman, 2007). It is estimated that rice production has to be increased by 56% over the next 30 years (Bouman *et al.*, 2002). Therefore, it is essential to 'produce more rice with less water' (Bouman, 2007; Guerra, 1998). Farmers apply 1200–1400 mm water to meet the higher (3–5.5 mm/day) evapotranspiration demand during the growing period of summer rice and more than 60% of this is met through ground water (Sarkar, 2001). Besides that, crop water productivity (water use per unit production of grain) of rice has also been reported to be much lower (0.6–1.6 kg/m^3) than that of other cereals such as maize and wheat (Zwart and Bastiaanssen, 2004).

Total amount of water rendered to the rice plant by sprinkler throughout the entire season was 1015 mm and total grain yield was 3,412 kg/ha. Contrary to that, with tube well irrigation, conventional flood irrigation method was used to cultivate the crop covering 631 ft^2 which showed that the total amount of water applied to rice field was 1435 mm compared to 1015 mm under sprinkler irrigation method. This translates to 30% less water consumption in sprinkler mehthod while meeting the rice water requirements. Same plant height and grain yields were observed in both tube well and the sprinkler irrigated fields. So there is no significant difference observed in rice yield 3,582 kg/ha in both fields, however significant water saving of 30% was observed in case of sprinkler irrigation method.

3.12 Dissemination of Research Results

The research results were disseminated by (a) organizing a Workshop/ Seminar on arsenic testing and identification of arsenic contaminated soils and ground water, (b) presenting articles in national and international conferences, (c) publication in research journals.

3.12.1 Awareness seminar/workshop

One day Workshop and Training on "Blanket testing of Arsenic and Fluoride, Using Field Kits and Effective Measure of Groundwater Pollution Identification and Remediation" was organized at the Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, on July 31, 2017. The objective of the workshop was to demonstrate arsenic testing of soils and groundwater with the use of field kit. It was also intended to bring awareness about the techniques used for identification of arsenic contaminated groundwater and possible remediation methods. The workshop was attended by students and faculty of Quaid-i-Azam University, Bahria University, International Islamic University and Punjab University. The workshop was also attended by officials of various organizations such as Pakistan Water Partnership (PWP), Hisaar Foundation, Sustainable Development Policy Institute (SDPI), Pakistan Institute of Nuclear Science and Technology (PINSTECH), Pakistan Council of Research in Water Resources (PCRWR). Dr. Muhammad Ashraf, Chairman PCRWR was the Chief Guest on the occasion.

3.12.2 Papers presented in conferences

The Project Co-PI and PhD scholar (Environmental Sciences), Asif Javed, presented two papers:

1. The paper titled "Spatial variation of arsenic in irrigation well water from three flood plains (Ravi, Chenab and Jhelum) of Punjab, Pakistan" was presented in an International Congress and Exhibition on Arsenic in the Environment, Environmental Arsenic in a Changing World (As2018), held in Beijing from 1-5 July 2018. The travel was funded by HEC.

2. The paper titled “Arsenic contamination of paddy rice fields” was presented in one day workshop on “Effective measure for ground water pollution and identification and remediation” that was held on 11 May 2017, at the Department of Environmental Sciences, Quaid-i-Azam University, Islamabad.

3.12.3 Research papers (in progress)

1. Research paper titled “Soil arsenic but not rice arsenic concentrations increasing with irrigation water arsenic in the Punjab Plains of Pakistan” is ready for submission.

2. Research paper titled “Arsenic fixation and mobilization in alluvial soils of Punjab under flooded irrigation system: Role of soil physic-chemical properties” is ready for submission.

3. Research paper titled “Non-saline ground water near the rivers, affected by the presence of toxic arsenic- A comparative appraisal of ground water quality for irrigation in the Punjab plains of Pakistan” is ready for submission.

3.13 Research Output

The details of research output are given below:

3.13.1 Student thesis completed

In this, project three M.Phil. and one PhD student were involved

3.13.1.1 M. Phil students

- Mr. Zakir Ullah Baig: Thesis topic was “Arsenic fixation and mobilization in alluvial soils of Punjab under flooded irrigation system: Role of soil physicochemical properties”.

- Mr. Danish Aziz: Thesis topic was “A comparative appraisal of irrigation water evolution in arsenic contaminated alluvial aquifers Punjab, Pakistan”.

- Mr. Rehman Ashraf: The thesis topic was “A water management practice to reduce bioavailability of arsenic in rice grain using sprinkler irrigation method in Punjab, Pakistan”

3.13.1.2 PhD thesis (near to submission)

1. Mr. Asif Javed: “Arsenic contamination of paddy rice fields: A study on geographic pattern in Punjab plains of Pakistan”

3.13.2 Book chapters

1. Javed, A., Baig, Z. U., Farooqi, A., and van Geen, A. 2018. Spatial variation of arsenic in irrigation well water from three flood plains (Ravi, Chenab and Jhelum) of Punjab, Pakistan. In *Environmental Arsenic in a Changing World: Proceedings of the 7th International Congress and Exhibition on Arsenic in the Environment (AS 2018), July 1-6, 2018, Beijing, PR China* (Vol. 50, p. 235). CRC Press. **(ISBN. 978-1-138-48609-6)**

4. CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

The problem of water scarcity in Pakistan is steadily worsening. Given the unreliability in the supply of canal water, farmers are increasingly relying on private tube wells, placing tremendous pressure on groundwater supplies. Overuse of groundwater and poor water management has led to the dropping of water tables in many areas; some studies indicate that the water table has gone down by more than 7 m in parts of the country. Agricultural technologies that conserve water without impairing production are therefore becoming increasingly important.

Rice is an obvious target for water conservation because of the amount of water it needs when cultivated under conventional methods. Failure to adapt to changing economic and environmental conditions can threaten Pakistan's position as a major rice exporting country. To help rice growers prepare for new challenges posed by changing environmental conditions farmers need to be encouraged to move away from traditional methods of cultivation that are heavy on the use of water and switch to the sprinkler system. This will help conserve water without compromising on the grain yield or quality. Equally importantly, it will help reduce arsenic levels in rice grown under aerobic environments and thereby significantly reduce concerns about chronic arsenic intoxication in exposed populations. At the same time it will allay any fear in the international market regarding the safety of rice exported from Pakistan.

4.2 Recommendations

Create awareness

- While finding safe water sources for irrigation is a long-term goal, there is an urgent need to raise awareness among the vulnerable population, regarding the hazards of arsenic in soil and water. Knowing the locations where arsenic concentrations is higher in their fields, i.e., in the top-soil near well heads, can help farmers make informed decisions about future cropping patterns, perhaps even shifting away from rice, taking into account potential loss of yield in the long run.

- Inform farmers and residents of the risks of using water containing elevated arsenic levels for drinking or cooking and the risk of direct ingestion of arsenic by children playing in contaminated rice fields. This will help residents protect their children from unnecessary exposure to arsenic, particularly in the Ravi flood plain.

Encourage mitigating actions

- Educate farmers/villagers in small-scale mitigation measures to reduce the accumulation of arsenic in the soil.
- The field kits used in this study for soil and water testing offer a quick, easy and cheap method for assessing arsenic levels in the soil and water. Tube well owners can be taught the use of these field kits to test well water and soil without depending on aid from outside agencies.

Switch to sprinkler irrigation

- Encourage farmers to switch to sprinkler irrigation where possible. Over a time period this will significantly reduce the concentration of arsenic in soil while helping conserve water—a pressing need of our time.

REFERENCES

Abedin, M.J., Cresser, M.S., Meharg, A.A., Feldmann, J. and Cotter-Howells, J. (2002a). As accumulation and metabolism in rice (*Oryza sativa* L.). *Environmental Science & Technology,* 36: 962-968.

Abedin, M.J., Feldmann, J. and Meharg, A.A. (2002b). Uptake kinetics of arsenic species in rice plants. *Plant Physiology,* 128(3): 1120-1128.

Acharyya, S.K. and Shah, B.A. (2007). Groundwater arsenic contamination affecting different geologic domains in India—a review: Influence of geological setting, fluvial geomorphology and quaternary stratigraphy. *Environmental Science and Health* Part A, 42(12): 1795-1805.

Adomako, E.E., Solaiman, A., Williams, P.N., Deacon, C., Rahman, G., Meharg, A.A. (2009). Enhanced transfer of arsenic to grain for Bangladesh grown rice compared to US and EU. Environment international 35, 476-479.

Ahmad, M.-u.-D., Turral, H., Masih, I., Giordano, M. and Masood, Z. (2007). Water saving technologies: Myths and realities revealed in Pakistan's rice-wheat systems. International Water Management Institute (IWMI).

Ahmad, N. 1983. Vertisols, Developments in Soil Science. *Elsevier*: 91-123.

Ahmed, Z.U., Panaullah, G.M., DeGloria, S.D. and Duxbury, J.M. (2011). Factors affecting paddy soil arsenic concentration in Bangladesh: Prediction and uncertainty of geostatistical risk mapping. *Science of the Total Environment,* 412: 324-335.

Ahsan, D.A., DelValls, T.A. and Blasco, J. (2009). Distribution of arsenic and trace metals in the floodplain agricultural soil of Bangladesh. *Bulletin of Environmental Contamination and Toxicology,* 82: 11-15.

Ali, M., Badruzzaman, A., Jalil, M., Hossain, M., Ahmed, M., Masud, A., Kamruzzaman, M. and Rahman, M. (2003). Fate of arsenic extracted with groundwater in fate of arsenic in the environment. *BUET*, 7-20.

Azad, M.A.K., Islam, M.N., Alam, A., Mahmud, H., Islam, M., Karim, M.R. and Rahman, M. (2009). As uptake and phytotoxicity of T-aman rice (*Oryza sativa* L.) grown in the As-amended soil of Bangladesh. *The Environmentalist*, 29: 436-440.

Baig, J.A., Kazi, T.G., Arain, M.B., Afridi, H.I., Kandhro, G.A., Sarfraz, R.A., Jamal, M.K. and Shah, A.Q. (2009). Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan. *Hazardous Materials,* 166: 662-669.

Barker, R., Dawe, D., Tuong, T., Bhuiyan, S. and Guerra, L. (1999). The outlook for water resources in the year 2020: Challenges for research on water management in rice production. *Southeast Asia,* 1, pp. 1-5.

Belder, P., Bouman, B., Cabangon, R., Guoan, L., Quilang, E., Yuanhua, L., Spiertz, J. and Tuong, T. (2004). Effect of water-saving irrigation on rice yield and water use in typical lowland conditions in Asia. *Agricultural Water Management*, 65: 193-210.

Berg, M., Stengel, C., Trang, P.T.K., Viet, P.H., Sampson, M.L., Leng, M., Samreth, S. and Fredericks, D. (2007). Magnitude of arsenic pollution in the Mekong and Red River Deltas—Cambodia and Vietnam. *Science of the Total Environment,* 372: 413-425.

Bhattacharya, P., Samal, A., Majumdar, J., and Santra, S. (2010). Accumulation of arsenic and its distribution in rice plant (*Oryza sativa* L.) in Gangetic West Bengal, India. *Paddy and Water Environment.* 8: 63-70.

Bogdan, K. and Schenk, M.K. (2009). Evaluation of soil characteristics potentially affecting arsenic concentration in paddy rice (*Oryza sativa* L.). *Environmental Pollution*, 157: 2617-2621.

Bouman, B. (2007). A conceptual framework for the improvement of crop water productivity at different spatial scales. *Agricultural Systems*, 93: 43-60.

Bouman, B., Humphreys, E., Tuong, T. and Barker, R. (2007). Rice and water. *Advances in Agronomy,* 92: 187-237.

Bouman, B., Wang, H., Yang, X., Zhao, J., and Wang, C. (2002). Aerobic rice (Han Dao): A new way of growing rice in water-short areas, *Proceedings of the 12th International Soil Conservation Organization Conference*. Tsinghua University Press Beijing, China: 31.

Brahman, K.D., Kazi, T.G., Afridi, H.I., Naseem, S., Arain, S.S. and Ullah, N. (2013). Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub districts of Tharparkar, Pakistan: A multivariate study. *Water Research*, 47: 1005-1020.

Buschmann, J., Berg, M., Stengel, C., *et al.* (2007). Arsenic and manganese contamination of drinking water resources in Cambodia: Coincidence of risk areas with low relief topography. *Environmental Science & Technology* 41: 2146-2152.

Chakraborti, D., Rahman, M.M., Das, B., Murrill, M., Dey, S., Mukherjee, S.C., Dhar, R.K., Biswas, B.K., Chowdhury, U.K. and Roy, S. (2010). Status of groundwater arsenic contamination in Bangladesh: A 14-year study report. *Water Research*, 44: 5789-5802.

Cheng, Z., Zheng, Y., Mortlock, R. and Van Geen, A. (2004). Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry. *Analytical and Bioanalytical Chemistry*, 379: 512-518.

Chowdhury, M.T.A., Deacon, C.M., Jones, G.D., Huq, S.I., Williams, P.N., Hoque, A.M., Winkel, L.H., Price, A.H., Norton, G.J. and Meharg, A.A. (2017). As in Bangladeshi soils related to physiographic region, paddy management, and mirco- and macro-elemental status. *Science of the Total Environment*, 590: 406-415.

Dawe, D. (1998). Water supply and research for food security in Asia, *Proceeding of the Workshop on Increasing Water Productivity and Efficiency in Rice-Based System*, July 1998. IRRI.

Deng, D., Wu, S.-C., Wu, F.-Y., Deng, H. and Wong, M.-H. (2010). Effects of root anatomy and Fe plaque on arsenic uptake by rice seedlings grown in solution culture. *Environmental Pollution,* 158: 2589-2595.

Dittmar, J., Voegelin, A., Roberts, L.C., Hug, S.J., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M. and Kretzschmar, R. (2007). Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 2. Paddy soil. *Environmental Science & Technology*, 41: 5967-5972.

Dittmar, J., Voegelin, A., Roberts, L.C., Hug, S.J., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M. and Kretzschmar, R. (2010). As accumulation in a paddy field in Bangladesh: Seasonal dynamics and trends over a three-year monitoring period. *Environmental Science & Technology,* 44:2925-2931.

Duxbury, J.M., Panaullah, G., Zavala, Y.J., Loeppert, R.H. and Ahmed, Z.U. (2009). Impact of use of As-contaminated groundwater on soil As content and paddy rice production in Bangladesh. *Food and Fertilizer Technology Center. Tech Bull,* 180: 1-11.

Erenstein, O. (2010). A comparative analysis of rice–wheat systems in Indian Haryana and Pakistan Punjab. *Land Use Policy,* 27: 869-879.

Farooqi, A., Masuda, H. and Firdous, N. (2007a). Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. *Environmental Pollution,* 145: 839-849.

Farooqi, A., Masuda, H., Kusakabe, M., Naseem, M. and Firdous, N. (2007b). Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. *Geochemical Journal,* 41: 213-234.

Fendorf, S., Michael, H.A. and Van Geen, A. (2010). Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. *Science*, 328: 1123-1127.

Feng, L., Bouman, B., Tuong, T., Cabangon, R., Li, Y., Lu, G. and Feng, Y. (2007). Exploring options to grow rice using less water in northern China using a modelling approach: I. Field experiments and model evaluation. *Agricultural Water Management,* 88: 1-13.

Fitz, W.J. and Wenzel, W.W. (2002). As transformations in the soil–rhizosphere–plant system: Fundamentals and potential application to phytoremediation. *Journal of Biotechnology,* 99: 259-278.

Fu, Y., Chen, M., Bi, X., He, Y., Ren, L., Xiang, W., Qiao, S., Yan, S., Li, Z. and Ma, Z. (2011). Occurrence of arsenic in brown rice and its relationship to soil properties from Hainan Island, China. *Environmental Pollution*, 159: 1757-1762.

George, C.M., Zheng, Y., Graziano, J.H., Rasul, S.B., Hossain, Z., Mey, J.L. and Van Geen, A. (2012). Evaluation of an arsenic test kit for rapid well screening in Bangladesh. *Environmental Science & Technology,* 46: 11213-11219.

GOP. (2016). Chapter on Agriculture. Government of Pakistan.

Guerra, L.C. (1998). Producing more rice with less water from irrigated systems. (vol. 5) IWMI.

Gupta, R.K., Naresh, R., Hobbs, P.R. and Ladha, J. (2002). Adopting conservation agriculture in the rice-wheat system of the Indo-Gangetic Plains: New opportunities for saving water, water wise rice production. *Proceedings of the International Workshop on Water Wise Rice Production*, April 8-11, 2002, Los Banos, Philippines: 207-222.

Hafeez, M., Bundschuh, J. and Mushtaq, S. (2014). Exploring synergies and tradeoffs: Energy, water, and economic implications of water reuse in rice-based irrigation systems. *Applied Energy,* 114: 889-900.

Hall, K.D., Guo, J., Dore, M. and Chow, C.C. (2009). The progressive increase of food waste in America and its environmental impact. PloS one 4(11): e7940.

Hassan, G.Z. and Bhutta, M.N. (1996). A water balance model to estimate groundwater recharge in Rechna Doab, Pakistan. *Irrigation and Drainage Systems,* 10: 297-317.

He, J. and Charlet, L. (2013). A review of arsenic presence in China drinking water. *Journal of Hydrology,* 492: 79-88.

HEC/USAID, (2016). Understanding the mechanism of As and fluoride and reducing exposure by targeting low As and fluoride aquifers in rural Punjab, Pakistan.

Heikens, A., Panaullah, G.M. and Meharg, A.A. (2007). As behaviour from groundwater and soil to crops: Impacts on agriculture and food safety, *Reviews of Environmental Contamination and Toxicology, Springer*: 43-87.

Honma, T., Ohba, H., Kaneko-Kadokura, A., Makino, T., Nakamura, K. and Katou, H. (2016). Optimal soil Eh, pH, and water management for simultaneously minimizing arsenic and cadmium concentrations in rice grains. *Environmental Science & Technology* 50: 4178-4185.

Hoque, M.A., Hoque, M.M. and Ahmed, K.M. 2007. Declining groundwater level and aquifer dewatering in Dhaka metropolitan area, Bangladesh: Causes and quantification. *Hydrogeology Journal* 15: 1523-1534.

Hossain, M., Jahiruddin, M., Panaullah, G., Loeppert, R., Islam, M. and Duxbury, J. (2008). Spatial variability of arsenic concentration in soils and plants, and its relationship with iron, manganese and phosphorus. *Environmental Pollution,* 156: 739-744.

Huhmann, B.L., Harvey, C.F., Uddin, A., Choudhury, I., Ahmed, K.M., Duxbury, J.M., Bostick, B.C. and Van Geen, A. (2017). Field study of rice yield diminished by soil arsenic in Bangladesh. *Environmental Science & Technology,* 51: 11553-11560.

Hundal, H., Singh, K., Singh, D. and Kumar, R. (2013). As mobilization in alluvial soils of Punjab, North–West India under flood irrigation practices. *Environmental Earth Sciences,* 69: 1637-1648.

Islam, M., Jahiruddin, M. and Islam, S. (2004). Assessment of arsenic in the water-soil-plant systems in Gangetic floodplains of Bangladesh. *Asian J. Plant Sci.* 3: 489-493.

ISO. (1995). Soil Quality: Extraction of Trace Elements Soluble in Acqua Regia. ISO.

Jakariya, M., Vahter, M., Rahman, M., Wahed, M.A., Hore, S.K., Bhattacharya, P., Jacks, G. and Persson, L.Å. (2007). Screening of arsenic in tubewell water with field test kits: evaluation of the method from public health perspective. *Science of the Total Environment,* 379: 167-175.

Khan, M.A., Islam, M.R., Panaullah, G., Duxbury, J.M., Jahiruddin, M. and Loeppert, R.H. (2009). Fate of irrigation-water arsenic in rice soils of Bangladesh. *Plant and soil,* 322: 263-277.

Kijne, J.W., Barker, R. and Molden, D.J. (Eds.) (2003). Water productivity in agriculture: Limits and opportunities for improvement. (vol. 1) Cabi.

Korte, N.E. and Fernando, Q. (1991). A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Science and Technology,* 21: 1-39.

Kramar, U., Norra, S., Berner, Z., Kiczka, M. and Chandrasekharam, D. (2017). On the distribution and speciation of arsenic in the soil-plant-system of a rice field in West-Bengal, India: A μ-synchrotron techniques based case study. *Applied Geochemistry,* 77: 4-14.

Lampayan, R.M. and Bouman, B.A. (2005). Management strategies for saving water and increasing its productivity in lowland rice-based ecosystems.

Langford, A. (2005). Practical skills in forensic science. Pearson Education.

Lauren, J. and Duxbury, J. (2005). Management strategies to reduce arsenic uptake by rice Behavior of As in Aquifers, Soils and Plants. Conference Proceedings. International Symposium, Dhaka.

Lund, U. and Fobian, A. (1991). Pollution of two soils by arsenic, chromium and copper, Denmark. *Geoderma*, 49: 83-103.

Malik, A.H., Khan, Z.M., Mahmood, Q., Nasreen, S. and Bhatti, Z.A. (2009). Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries. *Journal of Hazardous Materials* 168: 1-12.

Meharg, A.A. and Rahman, M.M. (2003). As contamination of Bangladesh paddy field soils: Implications for rice contribution to arsenic consumption. *Environmental Science & Technology*, 37: 229-234.

Mei, X., Ye, Z. and Wong, M. (2009). The relationship of root porosity and radial oxygen loss on arsenic tolerance and uptake in rice grains and straw. *Environmental Pollution*, 157: 2550-2557.

MOE. (2016). Environmental Quality Standards for Soil Pollution. Ministry of Environment, Government of Japan.

Neumann, R.B., St. Vincent, A.P., Roberts, L.C., Badruzzaman, A.B.M., Ali, M.A. and Harvey, C.F. (2011). Rice field geochemistry and hydrology: An explanation for why groundwater irrigated fields in Bangladesh are net sinks of arsenic from groundwater. *Environmental Science & Technology,* 45: 2072-2078.

Nickson, R., McArthur, J., Shrestha, B., Kyaw-Myint, T. and Lowry, D. (2005). As and other drinking water quality issues, Muzaffargarh District, Pakistan. *Applied Geochemistry,* 20: 55-68.

Norra, S., Berner, Z., Agarwala, P., Wagner, F., Chandrasekharam, D. and Stüben, D. (2005). Impact of irrigation with As rich groundwater on soil and crops: A geochemical case study in West Bengal Delta Plain, India. *Applied Geochemistry*, 20: 1890-1906.

Panaullah, G.M., Alam, T., Hossain, M.B., Loeppert, R.H., Lauren, J.G., Meisner, C.A., Ahmed, Z.U. and Duxbury, J.M. (2009). As toxicity to rice (*Oryza sativa* L.) in Bangladesh. *Plant and Soil*, 317:31.

Parsons, C., Grabulosa, E.M., Pili, E., Floor, G.H., Roman-Ross, G. and Charlet, L. (2013). Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: Considerations for sample preparation and measurement conditions. *Journal of Hazardous Materials*, 262: 1213-1222.

PCRWR. (2014). As assessment in rice growing areas of Pakistan.

Peterson, M.C. (2005). Characterization and mobilization of arsenic in various contaminated materials. Doctoral Dissertation.

Polya, D., Gault, A., Diebe, N., Feldman, P., Rosenboom, J., Gilligan, E., Fredericks, D., Milton, A., Sampson, M. and Rowland, H. (2005). As hazard in shallow Cambodian groundwaters. *Mineralogical Magazine.* 69: 807-823.

Qureshi, A.S., McCornick, P.G., Sarwar, A. and Sharma, B.R. (2010). Challenges and prospects of sustainable groundwater management in the Indus Basin, Pakistan. *Water Resources Management* , 24: 1551-1569.

Qureshi, A.S., Shah, T. and Akhtar, M. (2003). The groundwater economy of Pakistan. IWMI.

Rabbani, U., Mahar, G., Siddique, A. and Fatmi, Z. (2017). Risk assessment for arsenic-contaminated groundwater along River Indus in Pakistan. *Environmental Geochemistry and Health*, 39: 179-190.

Radu, T. and Diamond, D. (2009). Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *Journal of Hazardous Materials,* 171: 1168-1171.

Rahaman, S., Sinha, A.C. and Mukhopadhyay, D. (2011). Effect of water regimes and organic matters on transport of arsenic in summer rice (*Oryza sativa* L.). *Journal of Environmental Sciences,* 23: 633-639.

Rasool, A., Farooqi, A., Masood, S. and Hussain, K. (2016). As in groundwater and its health risk assessment in drinking water of Mailsi, Punjab, Pakistan. *Human and Ecological Risk Assessment: An International Journal,* 22: 187-202.

Rauf, M., Hakim, M., Hanafi, M., Islam, M., Rahman, G. and Panaullah, G. (2011). Bioaccumulation of arsenic (As) and phosphorus by transplanting Aman rice in arsenic-contaminated clay soils. *Australian Journal of Crop Science*, 5: 1678.

Ravenscroft, P. (2001). Distribution of groundwater arsenic in Bangladesh related to geology, groundwater arsenic contamination in the Bengal Delta Plains of Bangladesh: *Proc. KTH-Dhaka University Seminar*, KTH Special Publication, TRITA-AMI Report: 41-56.

Richards, L. A. (Ed.). (2012). *Diagnosis and improvement of saline and alkali soils*. Scientific Publishers

Roberts, L.C., Hug, S.J., Dittmar, J., Voegelin, A., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M. and Kretzschmar, R. (2007). Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. *Irrigation water. Environmental Science & Technology,* 41: 5960-5966.

Rosegrant, M.W., Cai, X. and Cline, S.A. (2002). World water and food to 2025: Dealing with scarcity. Intl Food Policy Res Inst.

Sabater, S. and Tockner, K. (2009). Effects of hydrologic alterations on the ecological quality of river ecosystems. *Water Ccarcity in the Mediterranean.* Springer: 15-39.

Sadee, B.A., Foulkes, M.E. and Hill, S.J. (2016). A study of arsenic speciation in soil, irrigation water and plant tissue: A case study of the broad bean plant, Vicia faba. *Food Chemistry*, 210: 362-370.

Sadiq, M. (1997). As chemistry in soils: An overview of thermodynamic predictions and field observations. *Water, Air, and Soil Pollution*, 93: 117-136.

Saha, G.C. and Ali, M.A. (2007). Dynamics of arsenic in agricultural soils irrigated with arsenic contaminated groundwater in Bangladesh. *Science of the Total Environment,* 379(2-3): 180-189.

Sankararamakrishnan, N., Chauhan, D., Nickson, R., Tripathi, R. and Iyengar, L. (2008). Evaluation of two commercial field test kits used for screening of groundwater for arsenic in Northern India. *Science of the Total Environment*, 401: 162-167.

Sarkar, S. (2001). Effect of water stress on growth, productivity and water expense efficiency of summer rice. *The Indian Journal of Agricultural Sciences,* pp. 71.

Shackley, M.S. (2011). An introduction to X-ray fluorescence (XRF) analysis in archaeology. *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology. Springer*: 7-44.

Sharif, M., Davis, R., Steele, K., Kim, B., Hays, P., Kresse, T. and Fazio, J. (2008). Distribution and variability of redox zones controlling spatial variability of arsenic in the Mississippi River Valley alluvial aquifer, southeastern Arkansas. *Journal of Contaminant Hydrology,* 99: 49-67.

Shrivastava, A., Barla, A., Singh, S., Mandraha, S. and Bose, S. (2017). As contamination in agricultural soils of Bengal deltaic region of West Bengal and its higher assimilation in monsoon rice. *Journal of Hazardous Materials,* 324: 526-534.

Shukla, D.P., Dubey, C., Singh, N.P., Tajbakhsh, M. and Chaudhry, M. (2010). Sources and controls of As contamination in groundwater of Rajnandgaon and Kanker District, Chattisgarh Central India. *Journal of Hydrology,* 395: 49-66.

Smedley, P.L. and Kinniburgh, D. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17: 517-568.

Smedley, P.L. and Kinniburgh, D.G. (2001). Source and behavior of arsenic in natural waters. *United Nations Synthesis Report on Arsenic in Drinking Water*. World Health Organization, Geneva, Switzerland.

Stahl, M.O., Harvey, C.F., Van Geen, A., Sun, J., Thi Kim Trang, P., Mai Lan, V., Mai Phuong, T., Hung Viet, P. and Bostick, B.C. (2016). River bank geomorphology controls groundwater arsenic concentrations in aquifers adjacent to the Red River, Hanoi Vietnam. *Water Resources Research*, 52: 6321-6334.

Stroud, J.L., Norton, G.J., Islam, M.R., Dasgupta, T., White, R.P., Price, A.H., Meharg, A.A., McGrath, S.P. and Zhao, F.-J. (2011). The dynamics of arsenic in four paddy fields in the Bengal delta. *Environmental Pollution*, 159: 947-953.

Sultana, J., Farooqi, A. and Ali, U. (2014). As concentration variability, health risk assessment, and source identification using multivariate analysis in selected villages of public water system, Lahore, Pakistan. *Environmental Monitoring and Assessment,* 186: 1241-1251.

Syu, C.-H., Huang, C.-C., Jiang, P.-Y., Lee, C.-H. and Lee, D.-Y. (2015). As accumulation and speciation in rice grains influenced by arsenic phytotoxicity and rice genotypes grown in arsenic-elevated paddy soils. *Journal of Hazardous Materials*, 286: 179-186.

Talukder, A., Meisner, C., Sarkar, M. and Islam, M. (2011). Effect of water management, tillage options and phosphorus status on arsenic uptake in rice. *Ecotoxicology and Environmental Safety*, 74: 834-839.

Thakur, J.K., Thakur, R.K., Ramanathan, A., Kumar, M. and Singh, S.K. (2010). As contamination of groundwater in Nepal—an overview. *Water,* 3: 1-20.

Tripathi, R., Sharma, P. and Singh, S. (2005). Tilth index: An approach to optimize tillage in rice–wheat system. *Soil and Tillage Research*, 80: 125-137.

Tripathi, R.D., Tripathi, P., Dwivedi, S., Kumar, A., Mishra, A., Chauhan, P.S., Norton, G.J. and Nautiyal, C.S. (2014). Roles for root iron plaque in sequestration and uptake of heavy metals and metalloids in aquatic and wetland plants. *Metallomics,* 6: 1789-1800.

Tuong, T. and Bouman, B. (2003). Rice production in water-scarce environments. Water productivity in agriculture: *Limits and Opportunities for Improvement*, 1: 13-42.

van Geen, A., Farooqi, A., Kumar, A., Khattak, J.A., Mushtaq, N., Hussain, I., Ellis, T. and Singh, C.K. (2019). Field testing of over 30,000 wells for arsenic across 400 villages of the Punjab plains of Pakistan and India: Implications for prioritizing mitigation. *Science of the Total Environment.* 654: 1358-1363.

van Geen, A., Zheng, Y., Cheng, Z., He, Y., Dhar, R., Garnier, J., Rose, J., Seddique, A., Hoque, M. and Ahmed, K. (2006). Impact of irrigating rice paddies with groundwater containing arsenic in Bangladesh. *Science of the Total Environment*, 367: 769-777.

Walkley, A. 1947. A critical examination of a rapid method for determining organic carbon in soils—effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 63: 251-264.

Wang, S. and Mulligan, C.N. (2006). Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environmental Geochemistry and Health*, 28: 197-214.

Waseem, A., Arshad, J., Iqbal, F., Sajjad, A., Mehmood, Z. and Murtaza, G. (2014). Pollution status of Pakistan: A retrospective review on heavy metal contamination of water, soil, and vegetables. *BioMed Research International*.

Watts, M., O'Reilly, J., Marcilla, A., Shaw, R. and Ward, N. (2010). Field based speciation of arsenic in UK and Argentinean water samples. *Environmental Geochemistry and Health,* 32: 479-490.

Williams, P.N., Islam, M., Adomako, E., Raab, A., Hossain, S., Zhu, Y., Feldmann, J. and Meharg, A.A. (2006). Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. *Environmental Science & Technology*, 40: 4903-4908.

Williams, P.N., Villada, A., Deacon, C., Raab, A., Figuerola, J., Green, A.J., Feldmann, J. and Meharg, A.A. (2007). Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. *Environmental Science & Technology* 41: 6854-6859.

WorldBank. (2005a). Towards a More Effective Operational Response. Environment and Social Unit – South Asia Region; Water and Sanitation Program (WSP) – South and East Asia.

WorldBank. (2005b). Towards a More Effective Operational Response. Environment and Social Unit – South Asia Region; Water and Sanitation Program (WSP) – South and East Asia. II.

Xie, X., Wang, Y., Su, C., Li, J. and Li, M., (2012). Influence of irrigation practices on arsenic mobilization: evidence from isotope composition and Cl/Br ratios in groundwater from Datong Basin, northern China. *Journal of Hydrology*, 424: 37-47.

Xie, Z.M. and Huang, C.Y. (1998). Control of arsenic toxicity in rice plants grown on an arsenic-polluted paddy soil. *Communications in Soil Science and Plant Analysis*, 29: 2471-2477.

Xu, X., McGrath, S., Meharg, A. and Zhao, F. (2008). Growing rice aerobically markedly decreases arsenic accumulation. *Environmental Science & Technology*, 42: 5574-5579.

Zavala, Y.J. and Duxbury, J.M. (2008). As in rice: I. Estimating normal levels of total arsenic in rice grain. *Environmental Science & Technology*, 42: 3856-3860.

Zhao, F.-J., McGrath, S.P. and Meharg, A.A. (2010). As as a food chain contaminant:mechanisms of plant uptake and metabolism and mitigation strategies. *Annual Review of Plant Biology*, 61: 535-559.

Zhao, F., Ma, J., Meharg, A. and McGrath, S. (2009). As uptake and metabolism in plants. *New Phytologist,* 181: 777-794.

Zwart, S.J. and Bastiaanssen, W.G. (2004). Review of measured crop water productivity values for irrigated wheat, rice, cotton and maize. *Agricultural Water Management*, 69: 115-133.

About the Authors

Dr. Abida Farooqi has more than 10 years of research and teaching experience with national and international research and academic institutes in the field of Geochemistry and is pioneer geo-chemist working on arsenic (As) pollution of ground water in Pakistan. Currently she is working as an Assistant Professor at Environmental Sciences Department, Quaid-i-Azam University, Islamabad. She holds PhD from Osaka City University Japan in field of Environmental Geochemistry. Her research work is focused on water quality related issues, especially arsenic and fluoride pollution of groundwater in rural and urban areas and its mitigation. She is working in close collaboration with many arsenic affected countries like Bangladesh, India, China and Myanmar for tackling the As problem in South and Southeast Asia. Dr. Farooqi has published more than 50 papers in reputed international journals.

Dr. Alexander van Geen is a Research Professor at Lamont-Doherty Earth Observatory (LDEO), Columbia University, New York, USA. His research interests range from Chemical Oceanography to Paleoceanography. He has increasingly turned his focus on the interactions between the environment and human health. The theme that runs through his on-going projects is that the study of the patterns of contamination, e.g. arsenic (As) in well water of across South Asia or lead (Pb) in soil contaminated with mine tailings in the Peruvian Andes, are spatially highly variable. He is a firm believer in the more widespread use of field kits by non-specialists to reduce exposure to environmental toxins, particularly in developing countries. Dr. van Geen has published over 400 peer-reviewed papers.

Asif Javed is serving as Senior Assistant Professor at the Department of Earth and Environmental Sciences, Bahria University, Islamabad, Pakistan. he has also served as Assistant Director, Water Management for more than 3 years after which he joined Bahria University in 2008. Mr. Javed holds MS in Environmental Information System (University of Greenwich, UK) and currently a PhD scholar at Quaid-I-Azam University Islamabad, Pakistan. His research interests include; contaminant hydrology; geochemistry and hydrology, with a special focus on exposure to arsenic (As) from drinking well water and uptake through food, rice in particular.

Main thrust of Applied Research component of the Water Center is to stimulate an environment that promotes multi-disciplinary research within the broader context of water-development nexus to support evidence-based policy making in the water sector. This is pursued using the framework provided by the six targets of the Sustainable Development Goal on Water i.e. SDG-6.

Contact:

U.S.-Pakistan Centers for Advanced Studies in Water

Mehran University of Engineering and Technology, Jamshoro-76062, Sindh - Pakistan

92 22 210 9145 water.muet.edu.pk /USPCASW /USPCASW