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Mini Review Article

Efficacy of Supported Metal Nanocatalyst – Synthesis of Potent Organic Compounds in Last Decade

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Introduction

The skill of achieving effective chemical reaction by applying innovative techniques which mainly concentrates on environmental aspects avoiding toxic and costly reagents represents a fundamental target of modern organic synthesis. The new era of chemistry is shifting towards the path of Nanocatalysis which is widening and becoming indispensible disciplines of Green chemistry for organic reactions. Over the last decade, the use of transition metal nanoparticles as catalysts is of great interest in both academia and industry, not only due to their very large surface areas producing high catalytic activity, but also due to their quantum size effect that sometimes shows high activity and unique selectivity [1]. The field of green organic synthesis has lately embraced various innovative scientific developments accompanied by improved and effective synthetic practices that avoid the use of toxic reagents and reactants.

The tuning of important organic transformations and this newer generation of nanocatalysts, worked together very well together to achieve important products. Because of their great differences from single molecules and bulk materials, nanoscale materials, including colloids, have attracted much attention since the last decade, especially recently, several reports have shown that homogeneous metal complex-catalyzed reactions can be conducted by using immobilized metal NP as catalytic systems with the advantages of the heterogeneous catalysts [2]. Because sustainable development involves the utilisation of reusable catalysts, the search for new catalytic systems to replace existing homogeneous ones is an important issue. There are some notable advantages of solid supported nanocatalyst for example: (i) reactions work well under mild conditions often in water; (ii) reactions are often very selective and tolerate a wide range of substrates (iii) the catalysts can be easily separated by filtration or magnetic decantation and reused many times with little variation of yield. This review will present in a nutshell recent findings on the use of nanoparticles supported on chemically robust solid materials.

2. Reactions using supported metal nanocatalyst: A review

Nezhadz and his group have reported a heterogeneous catalytic system based on the immobilization of Pd nanoparticles on a silica–starch substrate (PNP–SSS) [3a]. The PNP–SSS was found to be highly efficient recyclable catalyst for Heck Coupling and copper-free Sonogashira reaction in aqueous media by using K_2CO_3 as weak base. The silica–starch substrate (SSS) stabilized the Pd nanoparticles effectively and provided a matrix to prevent the aggregation of nanoparticles and their separation from the substrate surface. The catalyst was recovered by simple filtration and can be reused more than six times with little variation of yield.



 $Y = CO_2Et$, Ph, 4-Br-Ph, $CO(CH_2)_3Me$

Kalbasi *et al.* have prepared nickel nanoparticle-polyvinylamine (PVAm)/SBA-15, a polymerinorganic hybrid composite [3b]. This heterogeneous catalyst was efficiently used for the reduction of aromatic nitro compounds in the presence of NaBH₄ as a reducing agent in water at room temperature. The catalyst was removed easily from the medium easily upon completion of the reactions, and reused for several cycles without a decrease in catalytic activity.



where R = H, 2-Me, 3-OH, 4-OH, 3-NH₂, 4-NH₂ etc.

An efficient and cost-effective Cu-catalyzed O-arylation [4a]. was carried out by Hsieh *et al.* by involving phenols with iodoarenes to afford various substituted diaryl ethers derivatives with tiny loading of Cu_2O and 1*H*-imidazole-4-carboxylic acid as catalytic system under mild conditions, which provided good to excellent yields with good tolerance of functional groups.



K. Pitchumani and his workers have reported hydration of nitriles to amides in aqueous media catalysed by hydrotalcite-clay supported nickel nanoparticles(Ni-NP-HT) [4b]. Synthesized nickel nanoparticles were characterized by UV-DRS, powder XRD, SEM and HRTEM and Ni NPs/HT system was found to be effective for the synthesis of a variety of amides. Due to their unique properties such as reusability, ease of handling and cost effectiveness the heterogeneous catalyst was found to be more efficient than the conventional one. The catalyst can also be reused with only marginal decrease in its activity.



Chemoselective and eco-compatible reduction of aromatic nitroarenes in aqueous medium at ambient temperature have been developed by Layek *et al.* using Au(0) nanoparticles on MgO support [4c]

Various sensitive functional groups like allyl, alkoxycarbonyl, oxo, chloro, bromo, amine and nitrile

were tolerated in the aforesaid method. No additives or promoters was needed except only sodium borohydride as the source of hydrogen for the present protocol. The UV-visible spectrophotometric studies on 4-nitrophenol were also performed and an apparent rate constant of 7.6×10^{-3} s⁻¹ was obtained for this catalytic system [NAP-Mg–Au(0)].



Where R = H, Cl, Br, I, Me, OMe, NO₂, NH₂, CN, OH, OCOMe, allyl

Copper nanoparticles (mainly as Cu_2O) on titania support have been efficiently prepared by F. Alonso and his group which can catalyze the multicomponent reaction of propargylamines using aldehydes, amines, and alkynes (A³ coupling) at 70°C under solvent-free conditions.4d A wide range of structurally different propargylamines have been synthesized in moderate to excellent yields. The catalyst can be recycled with negligible leaching.

$$\begin{array}{c} O \\ R^{1} \stackrel{}{\longleftarrow} H \end{array} + \begin{array}{c} R^{2} \stackrel{}{\underset{H}{}} \stackrel{R^{3}}{\underset{H}{}} + \end{array} = R^{4} \end{array} \xrightarrow[\text{neat, 70 °C} \end{array} \xrightarrow[R^{2} \stackrel{}{\underset{R^{1}}{}} \stackrel{R^{3}}{\underset{R^{1}}{}} \xrightarrow[R^{4} \\ \end{array}$$

Where R^1 , R^2 , R^3 , R^4 = alkyl, aryl, cycloalkyl etc.

Shimizu and his co-worker have developed [5a] a heterogeneous and noble-metal-free catalytic system involving Al_2O_3 -supported Ni nanoparticles and which can be efficiently used for conversion of alcohols into primary amines under mild condition. Several aliphatic alcohols were well tolerated in the aforesaid protocol. Studies on the structure-activity relationship have shown that the surface metallic Ni⁰ species and co-presence of acid-base sites of alumina was responsible for the high activity.

$$\begin{array}{c} R_{1} \\ \searrow \\ R_{2} \\ 0.4 \text{ MPa} \end{array} \xrightarrow{\text{Ni} / \text{Al}_{2}\text{O}_{3} (1 \text{ mol}\%)} \\ \begin{array}{c} R_{1} \\ \swarrow \\ 140\text{-}146 \text{ }^{\circ}\text{C} \\ \end{array} \xrightarrow{R_{2}} \\ \begin{array}{c} R_{1} \\ \swarrow \\ R_{2} \\ \end{array} \xrightarrow{\text{NH}_{2}} \\ \end{array}$$

An efficient cycloisomerization of 2-alkynylanilines to biologically and pharmaceutically important indole moieties catalyzed by carbon-supported gold nanoparticles have been carried out by. J. Helaja *et al.*[5b] A wide range of diversely substituted indoles (both electron rich and electron deficient) can be synthesised with excellent yield.



Where R = *n*-propyl, Ph, C₆F₅, *p*-MeC₆H₄, *p*-OMeC₆H₄, *o*-NH₂C₆H₄, *p*-NH₂C₆H₄, *p*-NO₂C₆H₄, *p*-(CH₃CO₂)C₆H₄, *o*-pyridine etc. R¹ = H, 4-Cl, 5-Cl

Sureshbabu and his co-workers prepared an efficient Pd^0 nanoparticles supported on polyvinyl chloride (PVC) by the reduction of $PdCl_2$ by using sodium formate and NaOH in the ethanol–water system at reflux condition [6a]. The PVC supported Pd nanoparticles were successfully employed as effective catalyst for the cross coupling reactions, like Heck and Sonogashira coupling.



Where $R^1 = H$, Me, n-Bu, OMe, NO₂; $R^2 = H$, Me; X = I or Br



Where R = H, Me, OMe, NO₂, CN, CI etc.

A bimetallic nanosized Ce–Sm/SiO₂ catalyst have been developed by Reddy *et al* [6b]. It acted as an efficient catalyst to oxidise selectivity benzylamines into dibenzylimine derivatives with O_2 as the green oxidant under solvent-free conditions. Substrates with electron withdrawing as well as electron donating substituents readily reacted into this reaction.

$$R \xrightarrow{I_1} NH_2 \xrightarrow{Ce-Sm_2 / SiO_2} R \xrightarrow{I_1} N \xrightarrow{R} R$$

Where = H, Me, OMe, Cl, F

An efficient protocol of cyanation of aryl bromides and chlorides has been developed by Ranu *et al.* using palladium nanoparticles supported on ZnO [6c]. The protocol was ligand-, base-, and additive-free. A wide range of important nitriles including heterocyclic ones were synthesised by this method.

$$R-X$$
 + $K_4[Fe(CN)_6$ $\xrightarrow{ZnO-Pd NPs}$ $R-CN$
 DMF , 130 °C
 $X = Br, Cl; R = aryl, heteroaryl, styryl$

Branco and his group [6d] synthesised nanocat-Fe–Pd by using inexpensive precursors through immobilization of Pd on the magnetite surface and this was successfully employed as a catalyst in Buchwald–Hartwig reaction. Several sensitive functional groups like -Br, -NO₂, -COCH₃ were well tolerated during the reaction. Due to small Pd leaching, the catalyst was reused and recycled several times without any significant loss in catalytic activity.



Nasrollahzadeh *et al.* prepared the phosphine-free heterogeneous palladium catalyst [PS-TET-Pd(II)] which was a highly efficient and stable catalyst for the Sonogashira coupling reaction in water [6e]. This simple synthetic method has the advantages of high yields, elimination of toxic organic solvents and expensive, unstable and poisonous ligands, and easy work-up. PS-TET-Pd(II) is an eco-friendly catalyst because it can be easily recovered and reused without any significant loss of activity.



Where R = H, Me, OMe, NO₂, CN, CI etc. X= I, Br

Bhowmik and his group efficiently loaded a high concentration of air stable Ni(0) nanoparticles of average size 11 nm on reduced graphene oxide [6f]. Kumada–Corriu cross-coupling reactions have successfully carried out by this reusable heterogeneous catalyst (Ni/RGO-40). This catalyst was found to be equally active for the oxidative addition to the sp² C–F bond which was the attractiveness of the present protocol than the earlier reports. X-ray diffraction (XRD) and Raman spectroscopy studies on recovered catalyst were also done.



Where $R_1 = H$, Me, OMe, F, Cl, Br, I; $R_2 = H$, OMe; X = F, Cl, Br, I etc.

A cost-effective, operationally simple and eco-friendly protocol for the O-arylation of phenols with aryl halides under ambient atmosphere in aqueous medium has been developed by Ghatak *et al.* using alumina-supported nickel nanoparticles as an efficient, recyclable and stable heterogeneous catalyst [6g]. The reactions neither necessitate any ligand nor any inert environment. The present protocol for Ullmann coupling is highly chemoselective where more nucleophilc aromatic NH_2 and alcoholic OH groups remain unaffected. Chemically susceptible motifs like allyl, alkoxycarbonyl, formyl, oxo and nitro are well tolerated during the reaction. Thus the present study has developed a green method for chemoselective Ullmann coupling under aqueous medium using easily accessible, economically viable, highly stable and recyclable supported metal nanocatalyst with greater merits and wider applicability compared to many earlier reports.



Berrichi *et al.* prepared an efficient heterogeneous supported nano gold catalyst regularly distributed on ceria (Au/CeO₂) which was used [7a] to synthesize structurally important propargylamines via a one-pot, three-component coupling reaction of terminal alkynes, CH₂Cl₂, and different secondary amines. The catalyst was thoroughly characterized by XRD, TEM and DR-UV visible spectroscopy. The C–H bond of a terminal alkyne and the C–Cl bond of CH₂Cl₂ were actually activated by these supported gold nanoparticles. The catalyst can be recycled successfully up to three times.

An efficient, stable and solid palladium nanoparticles supported into a synthetic clay laponite have been prepared by Martínez *et al* [7b]. These solids was utilised as reusable catalysts in a Mizoroki–Heck reaction under solvent free conditions. Et₃N was used as a mild base in the reaction. The catalysts were efficiently recovered by extracting reaction products with an auxiliary solvent.



A single-site Pd(II) catalyst was developed by where 2,2'-bipyridine-grafted periodic mesoporous organosilica (PMO) was employed as the support of a Pd(II) complex [7c]. The overall performance of the single-site Pd(II) catalyst in the oxidative Heck reaction was investigated. The investigation results show that the catalyst displays over 99% selectivity for the product formation with high reaction yield. X-ray absorption spectroscopy reveals that the catalyst has remarkable lifetime and recyclability.



Bora *et al.* have synthesised an eco-compatible, efficient and reusable Mont K-10 supported AgNPs as catalyst and developed a methodology for the ipso-hydroxylation of arylboronic acids and their derivatives to phenols using aqueous hydrogen peroxide as oxidant by it [7d]. Ligand, base and solvent-free condition and broad functional group compatibility as well as short reaction time made this methodology quite attractive.



R = H, Me, CMe₃, OMe, CI, F, CHO, CN, NO₂, CF₃

The catalytic activity of palladium supported on magnetic nanoparticles in the amination coupling reaction of different nitrogen containing substrates with aryl halides has been investigated [8a]. C–N bond formation was achieved in this protocol and the catalyst could be separated by magnetic decantation. Good to high yields of products with excellent functional group tolerance were found. Increasing the electron withdrawing nature of the substituents dramatically decreased the yield of the reaction probably due to a competitive dehalogenation reaction.



Rezaei *et al.* have synthesised a polystyrene-anchored cryptand 22-copper (I) iodide complex catalyst which was efficiently utilized as a heterogeneous catalyst for the cross-coupling reaction of thiols with aryl halides in aqueous media under aerobic conditions [8b]. The features of this methodology are oxygen and water insensitivity, low catalyst loading, ease of separation, and recyclability of the catalyst, as well as high yield of products and ability to tolerate a wide variety of substituted reactants.

ArX + RSH
$$\xrightarrow{\text{PS-C22-Cul (0.4 mol%)}}_{\text{DMF/H2O, K2CO3, 90 °C}}$$
 ArSR
Ar = Ph, 4-NO₂C₆H₄, 4-MeOC₆H₄, 4-H₂NC₆H₄ etc
X = I, Br, Cl
R = Ph, 4-MeC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄etc

A new series of imine–Pd–(N-heterocyclic carbene) complexes have been developed as efficient catalysts for Pd-catalyzed Suzuki–Miyaura coupling reaction.[8c] Based on the performance of supporting ligands, correlation of structure and catalytic activity has been demonstrated via experimental and computational modelling and DFT computations. A broad reaction scope of aryl and heteroaromatic chlorides could proceed at extremely low catalyst loading (minimum 0.005 mol %).



Borah *et al.* have reported for the a green synthesis of Cu₂O nanoparticles using biogenic route with *Musa balbisiana colla* fruit extracts and developed a new reusable and heterogeneous catalytic system for the effective conversion of aryl and heteroaryl boronic acids via *ipso*hydroxylation using H_2O_2 as oxidant to phenols [9a]. The synthesized nanoparticles are characterized by SEM (Scanning Electron Microscope), TEM (Transmission Electron Microscope) and powder XRD (X-Ray Diffraction) methods. This protocol is more effective comparative to the earlier literature report due to short reaction time, high yield and reuse of the catalyst up to 5th cycle.



An effective and cheap method of biosynthesis of $Fe_2O_3@SiO_2$ nanocomposite has been developed using Zanthoxylum rhetsa [9b]. The supporting material i.e. SiO_2 which was extracted from rice paddy straw, waste material. Here, Tamuly and his co-worker have achieved a green, mild and ecofriendly protocol for ipso-hydroxylation of arylboronic acids to phenols without using H_2O_2 as oxidant in presence of biogenic $Fe_2O_3@SiO_2$ nanocatalyst and air at 50°C. It is very simple, cost effective and compatible with various electron donating as well as withdrawing groups.

$$R \xrightarrow{OH} OH \xrightarrow{Fe_2O_3 @ SiO_2} OH \xrightarrow{OH} OH$$

R = H, Me, CMe₃, OMe, CI, CHO, CN, NO₂

Tai *et al.* have developed the first synthesis and catalytic application of magnetically separable nanoparticles possessing mesoporous sulfonic acid functionalized silica shells [9c]. The choice of sulfonate grafting technology strongly adopts simultaneously sulfonic acid loadings and esterification activity, with hydrothermal saline promoted grafting doubling the specific activity with respect to the conventional grafting route. These porous nanocomposites afford super efficacy towards both facile recovery and re-use of the catalyst.

Indoles and Quinolines are both of the most widely used heterocyclic compounds in Nature, with many indole alkaloids possessing considerable pharmacological activity as they are extensively important in the field of agricultural and animal health, textiles, and perfume industry. Elumalai *et al.* have achieved that gold nanoclusters are good catalyst precursors for Au(0) nanoparticles which catalyse the dehydrogenation of indolines, tetrahydroquinazolines, and related *N*-heterocycles [10a].



R= H (5a, 85%), 6-Br (5b, 77%), 6,8-Br (5c, 45%)

A microwave-assisted method to produce benzaldehyde from styrene was described by using ferrite magnetic nanoparticles, MFe₂O₄ [M= Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺] as catalysts.[10b] The CoFe₂O₄ nanoparticles revealed the best catalytic performance towards the selective production of benzaldehyde selectively in 3h at 80 °C using *t*-BuOOH as oxidant. The best catalytic performance was obtained using CoFe₃O₄ followed by MnFe₃O₄ \ge CuFe₃O₄ > Fe₃O₄ > NiFe₃O₄ > ZnFe₃O₄



Wu *et al.* has described a novel and eco-compatible Au-based catalytic system for imine synthesis from the direct oxidative coupling of alcohol and amine under air atmosphere.[11a] It was also developed that the uniform and small Au nanoparticles in metallic state were active sites and responsible for activating and converting an alcohol to an aldehyde, i.e., the rate-determining step. The subsequent condensation of aldehyde with amine was found fast. Au nanoparticles loaded on Zn-doped V-Al₂O₃ was effective for the first time as selective and stable heterogeneous catalyst for synthesis of imine from the primary alcohols and amines.



Beller and his co-worker have described efficient cobalt-based nanocatalysts for general and selective hydrogenation of aromatic hydrocarbons to produce the corresponding aliphatic products, which serve as essential compounds in chemical and life science industries as well as for energy and material sciences.[11b] Key to success for this hydrogenating process is the graphitic shell-encapsulated cobalt nanoparticles prepared by the template synthesis of cobalt–PMA–PZ CP on commercial silica and subsequent pyrolysis under an inert atmosphere.



Au nanoparticles, generated by the metal vapor synthesis technique, were supported onto $Ce_2O(CO_3)_2$ ·H₂O, a crystalline, Ce^{3+} based inorganic material.[12a] Au XPs measurements confirmed the presence of only Au atoms in the metallic oxidation state on the NPs' surface. Aerobic allyl alcohol oxidation reactions conducted with the obtained heterogeneous catalyst in toluene showed: (i) A catalytic conversion of allyl alcohols to the unsaturated carbonyl compound (major compound) which is superior to that of Au@CeO₂, known as reference system for this kind of chemistry; (ii) A partial allyl alcohol isomerization activity to the corresponding saturated carbonyl compound, when the allyl group of the substrate is sterically not hindered, which contrasts results obtained with





A new reusable Pd-AcAc-Am-Fe₃O₄@SiO₂ nanomagnetic catalyst was efficiently developed and characterized using ATR-IR, TEM, FE-SEM, EDX, ICP-AES and VSM [12b.] The supremacy of the catalyst are simplicity, selectivity, eco-friendliness and ease of recovery using an external magnetic field. The recovered catalyst can be reused up to six cycles without significant loss of catalytic activity. The developed protocol extends many advantages such as high substrate tolerability, short reaction time, high yields and catalyst reusability.

3. Conclusions

This article is nothing but an attempt to compile the literature on application of nanocatalysts in organic synthesis. The correct and update citation and literature survey is immensely essential for chemists to find proper information, innovative ideas, and advancement of any discipline. The application of green protocol for the synthesis of various important organic frameworks has advantages such as moderate to high yield, short reaction time, and use of cheap chemicals, easy and operationally simple procedure. We firmly believe that the present mini review article may be lighting the prospective of application of nanocatalysis and uplift synthetic organic chemists in this field for the synthesis of organic compounds using nanoparticles.

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Skin lesions associated with chronic arsenic exposure through food chain is associated with GST and CYP 450 polymorphism

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Abstract:

Background: Arsenic contamination through food chain causes skin manifestations. However, the response varies widely among persons despite receiving similar level of arsenic for similar duration. Person may develop arsenical skin lesions or not despite of receiving similar level of exposure.

Method: Polymorphism in GST and CYP gene and their frequency distribution ratio may modify skin manifestations in persons receiving arsenic through food chain. Polymorphic variation of CYP450 and GST in 148 study subjects are evaluated. Subjects were recruited from one of major arsenic affected district, Nadia of West Bengal, India, having high arsenic content in their food. Exposed subjects were categorized into two groups, i.e, with arsenical skin lesions and with out arsenical skin lesions. Concentration of arsenic in their urine, hair, drinking water, food, extent of clinical manifestations, GST status and CYP status are determined.

Result: Results showed that genetic polymorphism of GSTM1 and T1 are significantly associated (p<0.05) with arsenic induced clinical symptoms. CYPIAI A/G transition and CYP c2c2 form are also significantly associated with (p<0.05) the severity of skin manifestations.Distribution ratio of A/G transition, c2c2 polymorphic variation of CYP and frequency of GSTM1 null and T1 null are significantly associated with arsenic induced skin manifestations.

Conclusion: Polymorphic variations of GST and CYP genes play important role in the arsenic induced skin manifestations in persons exposed chronically to environmental arsenic.

Keywords : Arsenic, genetic polymorphism, metabolism, skin lesion, food chain.

Introduction:

Humans are exposed to environmental arsenic mostly through drinking water. The subsoil water of many country of the world including India has been contaminated with arsenic. In India, the basin of river Ganga in West Bengal is highly contaminated with arsenic. The allowable limit for arsenic in drinking water set by the US protection Agency is $10 \mu g/l$. A large number of people, mostly living in rural and semi-urban areas of south eastern part of West Bengal drink subsoil water contaminated with arsenic at a much higher level and they experience various arsenic induced clinical manifestations. In very recent years general health awareness of the Indian people has been increased and people are switched over to surface water or alternative source for water for this purpose to avoid arsenic exposure through water in exposed areas. But in most of the cases it has been notified that still they have clinical manifestations. Urine examination had revealed a current exposure of arsenic in those people. It indicates that they are still receiving environmental arsenic through any alternative source, may be from food. The subsoil water which contains inorganic arsenic is

also used in irrigation purpose and therefore may be transmitted to plants and enter in to the food chain.

Recent evidence coming from Bangladesh, India, Combodia, Vietnam and other countries revealed that food grains can accumulate arsenic when harvested in arsenic contaminated soil and ground water [1,2,3]. Outcomes of recent research indicate that rice is the more potent accumulator of arsenic [3,4,5,6]. Paddy field flooded with arsenic contaminated ground water produces paddy containing significant amount of inorganic arsenic in it [7]. People of these arsenic contaminated areas are receiving food grains specifically rice, rich in arsenic. Live stock in this manner exposed to environmental arsenic is another alternative route of exposure to human [8, 9]. Food chain contamination therefore is a probable route of arsenic entry in human.

People who are receiving arsenic through these alternative routes are also experiencing clinical manifestations. GuhaMazumder and his group reported in a separate study that participants coming from arsenic endemic area of West Bengal have exposure of arsenic through food and the main component of dietary arsenic exposure is rice [10]. In the present report we are going to explore the association of polymorphic variation of genes with arsenic induced skin manifestations in persons with arsenic exposure through food. Subjects are selected from same arsenic endemic area and collection of samples and subject recruitment has been done during 2008-2009. Categorization has been made on the basis of skin lesions present or not (variable) where the degree of arsenic exposure is constant.

We observed in previous studies that people receiving same level of exposure with a similar duration may develop differential degree clinical manifestations. This type of interindividual variability in clinical responses may be due to underlying arsenic metabolism. Polycyclic aromatic hydrocarbons and environmental carcinogens and co-carcinogens are often metabolized to reactive DNA binding diol epoxides by phase I enzymes of Cytochrome P450 (CYP) family and detoxified by phase II enzymes, including Glutathione-S-Transferase (GST) [11,12]. This usually occurs before they reach their targets and several of these enzymes have been shown to be polymorphically distributed in human population. Induction of CYP 450 enzymes has been recognized after acute arsenic exposure and this may ascertain some direct or indirect role in arsenic metabolism.

Individual GST and CYP450 gene status, their polymorphic variation and frequency of distribution therefore may be responsible for the inter-individual variability in arsenic metabolism and susceptibility to disease. We are therefore trying to find out the relationship between polymorphism of CYP 450 and GST genes and arsenic induced skin manifestations after food chain contamination by arsenic. However, this is the first report of association of CYP450 gene polymorphism along with GST gene and skin lesions in persons chronically exposed to arsenic through their food chain in West Bengal, India.

Material and methods:

We have recruited a total 148 study subjects. The subjects were selected from arsenic affected districts of West Bengal for arsenic exposed people and unexposed area of West Bengal for arsenic unexposed people and the later group is recruited as control.

Drinking and cooking water samples, morning void urine samples and 24 hrs food samples had been collected to detect the concentration of arsenic in their drinking water, urine and in food.

The study subjects are categorised in three groups. In group I there are 53 subjects taken from arsenic exposed areas and all of the subjects have definitive skin manifestations. Selection criteria were presence of characteristic skin manifestations, viz., hyperpigmentation, hypopigmentation and keratosis [13,14]. The subjects of group II (n=62) have no skin manifestations although they have current exposure to arsenic reflecting in their urinary arsenic concentration. They had previous exposure to arsenic through their drinking water for years but now switched over to safe surface water. The average concentration of arsenic in raw rice in arsenic exposed population was 315µg/kg and the range of exposure of arsenic through food is 118-872 µg/kg [15]. Group III (n= 33) did not have any history of arsenic exposure from water or directly from food source. They are selected from non endemic area of West Bengal. The subjects take safe surface water (<50 µg/l) and have not any past exposure to arsenic. They are totally devoid of any kind of arsenical skin manifestations. They were treated as control in this study. History of arsenic exposure from each participant was obtained in detail including duration of water intake, food sampling and food arsenic concentration. All male participants were small traders or were involved in office jobs in small concerns.Women were housewives. Most men were smokers and women were all nonsmokers.

Written informed consent was obtained from all participants before drawing their blood. Ethical principles followed by the institute are guided by rules as formulated by Indian Council of Medical Research and these are in agreement with Helsinki rules. The name of the institute where human studies were carried out is Indian Institute of Chemical Biology (IICB) which is run by Govt. of India, a CSIR research Unit. The collection of Blood samples were carried out through field survey in arsenic exposed areas of southern portion of West Bengal by DNGM Research Foundation (DNGMRF) Kolkata, West Bengal.

Field Study:

Demographic data, social characteristics and occupational data were collected for each recruit. They were categorized as sedentary and moderate workers. Water samples for drinking and cooking, morning void urine sample and 24 hours food samples were collected for each participants and estimated for arsenic content and published earlier [16].

Collection of Blood samples:

EDTA anticoagulated blood samples were collected from different arsenic affected blocks of Nadia and kept at -20°C at DNGM research foundation, (DNGMRF), Kolkata. Blood samples were also collected from age and socio economic status matched arsenic unexposed subjects from arsenic unexposed areas. Exposed subjects were characterized as arsenicosis positive (group I) and arsenicosis negative (group II). All the blood samples were transported in icebox from DNGMRF to the Department of Physiology, Gene Regulation laboratory, IICB, Kolkata for further storage at -70°C and subsequent analysis after DNA extraction.

Clinical Symptom Score:

Each study subject has been given a clinical symptom score according to their skin manifestations. Both pigmentation and keratosis were graded 1,2 or 3, depending on the level of symptoms. Sum of the two was clinical symptom score, so that a person can have maximum score of 6. The control subjects have no pigmentation and keratosis and therefore clinical symptom score of 0 [17].

Determination of Arsenic in drinking water and urine

The concentration of arsenic in drinking water and urine was determined by atomic absorption spectrophotometry hydride generation (FI- AAS-HG) system according to manufacturer's instruction. Urine arsenic concentration was measured according to Das et al [18] using FI-HG-AAS (PerkinElmer A Analyst 200).

Genotyping of Glutathione- S-Transferase (GST) M1 and T1

In humans, five classes of GST genes exist: α (*GSTA*), μ (*GSTM*), π (*GSTP*), θ (*GSTT*), and ζ (*GSTZ*) with one or more genes in each class. The enzymes have different, but sometimes overlapping, substrate affinity [19].Genetic polymorphisms resulting in lack of enzyme activity due to homozygous deletion of the different subgroups GST gene. The polymorphic deletion of M1 and T1 gene was genotyped using the multiplex PCR approach [20].

Genotyping of Cyp IAI exon 7 and CYP 2E polymorphism:

Two functionally important nonsynonymous polymorphisms have been identified for CYP1A1 gene, a base substitution at codon 462 in exon 7, which is a A to G transition at position 2455 in the heme binding region of exon 7 resulting in substitution of isoleucine with valine (Ile462Val (exon 7), (National Center for Biotechnology Information single nucleotide polymorphism(SNP) identifier rs1048943; adenine (A) to guanine (G) substitution at nucleotide 2455(2455A.G)) and a point mutation [thymine (T) to cytosine (C)] at the MspI site in the 3'-untranslated region (rs4646903;3801T.C) [21]. The MspI restriction site polymorphism resulted in three genotypes: a predominant homozygous m1 allele without the MspI site (genotype A), the heterozygote (genotype B), and a homozygous rare m2 allele with the MspI site (genotype C). The exon 7 restriction site polymorphism resulted in three genotypes: a predominant homozygous (Ile/Ile) or A+G-, the heterozygote (Ile/Val) or A+G+, and the rare homozygous(Val/Val) or A-G+. CYP2E1 contains six restriction fragment length polymorphisms, of which the RsaI polymorphism (CYP2E1*5B; C-1054T substitution) is one. C-T substitution at Rsa I polymorphic site can create c1/c1 (wild type homozygous), c1/c2 (heterozygous with one T) and c2c2 (homozygous for T).

CYP A/G polymorphism: We studied an A to G transition in exon 7 of the CYPIAI gene that results in the substitution of value for isoleucine at residue 462. We assessed this polymorphism by the allele-specific PCR method [22]. PCR products of 322 bp were then subjected to electrophoresis in 1.8% agarose gel. Three polymorphic varieties A+G- (Ile/Ile), A-G+(val/val) and A+G+ (Ile/ val) have been found in our population.

CYP 1A1 (T/C) polymorphism : Genotyping of the 3'-end polymorphism of the CYPIAI gene (located at the 264th base downstream of the polyadenylation signal) was carried out by PCR amplification (340 bp) by the method described earlier [23, 24]. The amplification products were then digested with MspI and subjected to electrophoresis on a 1.8% agarose gel. The CYP1AI 'A' genotype is the predominant wild-type homozygote (340 bp PCR product, CYP T+C-, which remains undigested by Msp I). CYP 1AI 'C' obtained from Msp I digestion results to give 200 and 140 bp products, (CYP T-C+). Genotype B is heterozygous for both alleles where the Msp I digestion results in three bands 340bp, 200 bp and 140 bp, called CYP T+C+.

CYP 2E polymorphism: CYP2EI also exhibits several polymorphisms in the 5' flanking region of the gene. One of them includes two distinct base substitutions that are in genetic disequilibrium with each other and creates Rsal and PstI restriction sites [23, 25]. The PCR

product of 413 bp was then subjected to Rsa I digestion to yield 360 and 53 bp fragments for mutant allele (homozygous mutant) or a heterozygous mutant (413 bp. 360 bp and 53 bp). The sample having no base substitution in either allele doesn't shows any other fragments except the primary one (413 bp) after RsaI digestion. 413 bp undigested with Rsa I represents c1c1 wild type homozygous, 380 bp, 53bp are digested heterozygous respectively (c1c2, c2c2).

Statistical Analysis: Assuming non-normal distribution of data in various groups of genetic polymorphisms and arsenic exposure with and without skin manifestations we have done nonparametric statistics to find out the association between genetic polymorphism and arsenic induced skin manifestations [26]. We have analyzed the data by nonparametric Median test to find out the correlation between GSTMITI, CYPIAI A-G, CYP T-C, CYP2E polymorphism with the elimination of arsenic from the body as total urinary arsenic, occurrence of arsenic induced skin manifestations.

Result:

Demographic distribution and frequency of occurrence of different polymorphic variations has been tabulated in table 1 and 2 respectively.

In group I the occurrence of GSTMI null (M-T+) is 36% and GSTTI null (M+T-) is 12% (table 1). Both GSTMI null (p<0.01) and GSTTI null (p<0.05) genotype have a significantly low concentration of total urinary arsenic than the non-null counter part of the population in group I. In group II the occurrence of GST MI null is 27 % and GSTTI null is 7% (table 2). Total urinary arsenic is higher in GSTMI and TI non-null genotype than GSTMI and GST TI null genotype (p<0.05) in group II too. In group III the total urinary arsenic is not significantly high in GSTMI or GSTTI non null genotype in comparison to GSTMITI null genotype. The median value of clinical symptom score was significantly higher (p<0.01, p<0.05) in GSTMI and TI null genotype respectively in comparison to GSTMITI non null genotype of group I (table 3).

In our study population the occurrence of CYP A+G- genotype (Ile/Ile, also known as 2A wild type) is 26.65 %, A+G+ (Ile/Val, mutant) is 59.50%, and A-G+ (Val/Val, mutant) is 13.5% in group I (table 2). In group II the percentage of occurrence of A+G- is 18% and A+G+ is 66.5%, A-G+ is 15 %. In group III also the occurrence of A+G+ is 66.5%, A+G- is 18.5% A-G+ is 15 % (table 2). In group I the median values of skin manifestations is significantly higher (p<0.01) in A+G- population (Ile/Ile) in comparison to A+G+(Ile/Val) population. In A-G+ (Val/Val) population also there is a significantly lower (p<0.05) degree of skin manifestations in comparison to wild type A+G- population in group I (table 3).

Unlike group I, in group II there is no significant difference in respect to skin score between A+G-, A+G+ and A-G+ population. Total urinary arsenic is significantly lower in wild type A+G- population in comparison to mutant A+G+ in group I (p<0.01) and group II (p<0.001) (table 3). The total urinary arsenic is significantly higher in A-G+ genotypic variety in group I and II in comparison to A+G- polymorphic variety(p<0.05, p<0.01 respectively) (table 3).

Group name	Age (yrs)	Sex	Average Ht, Wt	Smoking habit	Occupation	Average duration of exposure	Food arsenic	Urine arsenic	Water Arsenic
GroupI Past water arsenic level 50- 500µg/l N=53	i). 20-35 N=18 ii). 35-50 N= 25 iii). 51-65 N= 10	i).M=12, F=6 ii).M=21, F=4 iii).M=6, F=4	M=Ht=159cmW t= 63kg Ht= 150 cm, Wt=51 kg	M= all smoker F= all non smoker	36 farmers, 3 small traders F=housewives	7 yrs.			
Group II 50- 500µg/l N=62	i). 20-35 N=12 ii). 35-50 N= 25 iii).51-65 N= 25	i).M=9, F=3 ii).M=21 F=4 iii).M=13, F=12	M=Ht= 159cm Wt= 63 kg F=Ht= 150 cm, Wt=51 kg	M= all smoker F= non smoker	32farmers, 10 small traders 1 service holder F=house wives	6 yrs			
Group III 0- 10μg/l N=33	i). 20-35 N=5 ii). 35-50 N= 15 iii).51-65 N= 13	i).M=5, F=0 ii).M=11 F=4 iii).M=10, F=3	M=Ht=164cm Wt= 65 kg F=Ht= 152 cm, Wt=52 kg	M= all smoker F= non smoker	M= 20 farmers, 5 small traders 1 service holder F=house wives	0 yrs.			

Table 1: Demographic distribution of study population in three cohort

Table 2 : Distribution of frequency of occurrence of different polymorphic variation in all three cohort

Group Name	GSTMITI	CYPIAI A/G	CYPIAIT/C	СҮР2Е
Group I	M+T+ 48% M-T+ 36% M+T- 12% M-T- 4%	A+G- (Ile/Ile) 26.65% A+G+(Ile/Val) 59.50% A-G+ (Val/Val) 13.5%	T+C- (A) 71.62% T-C+ (C) 13.44% T+C+ (B) 14.94%	c1c1 49% c1c2 19% c2c2 32%
Group II	M+T+ 63% M-T+ 27% M+T- 7% M-T- 3%	A+G- 18.50% A+G+ 66.50% A-G+ 15%	T+C- (A) 70 % T-C+ (C) 15% T+C+ (B) 15%	c1c1 67% c1c2 13% c2c2 20%
Group III	M+T+ 62.75% M-T+ 25.25% M+T- 9% M-T- 3%	A+G- 18.50% A+G+ 66.50% A-G+ 15.00%	T+C- (A) 79.33% T-C+ (C) 10% T+C+ (B) 10.67%	c1c1 63% c1c2 15% c2c2 22%

In case of CYP T- C polymorphism the frequency of occurrence of A genotype is 71.62% in group I, 70% in group II and 79.33% in group III. Occurrence of C genotype is 13.44% in group I, 15% in group II and 10% in group III. The frequency of B genotype is 14.94% in group I, 15% in group II and 10.67 in group III (table 2). The differences in total urinary arsenic between A and B genotype and between A and C genotype are not significant though

the median value of total urinary arsenic is higher in A genotype than B and C genotype in group I and II. No significant difference occurs in respect to skin score in these three genotypes of group I.

	GST	MITI	CYPL	AI A/G	CYF	PT/C	CYP 2E		
	Median Value of T.U A & skin score		Median skin scor	Median Value of T.U A & skin score		Median Value of T.U A & skin score		Median Value of T.U A & skin score	
	T.U.A	Skin Score	T.U.A	Skin Score	T.U.	Skin Score	T.U.As	Skin Score	
	M+T+ 197 M-T+ 84	2	A+G+ 203	2 p< 0.01	T+C- 89	2	c1c1 218	1	
	p<0.01 M+T- 107	4 7 p<0.01	A+G- 97	5	T+C+ 94	3	c1c2 128	1	
Group I	p<0.05 M-T- 96	2	p<0.01 A-G+	3	T-C+ 101	2	c2c2 117	3	
		3 p<0.05	107 p<0.05	p<0.05 4	p=0.6		p<0.01	p=0.06	
Group II	M+T+ 204 M-T+ 97	۰	A+G+ 169		T+C- 95		c1c1 241		
	p<0.01 M+T- 103	3	A+G- 89		T+C+ 97		c1c2 176		
	p<0.05 M-T- 79		p<0.01 A-G+		T-C+		c2c2 132		
			143 p<0.05		131	, p=0.053	p<0.05		
Group III	M+T+ 33 M-T+ 31		A+G+ 19		T+C- 12		c1c1 52		
	M+T- 12		A+G- 26		T+C+ 23		c1c2 49		
	М-Т	 	A-G+ 11		T-C+ 19		c2c2 23		

Table 3: Represents the Median value of Total urinary arsenic and Skin score i different polymorphic subgroups in three different groups

The CYP450 2E1 gene (CYP2E1) is located on chromosome 10q26.3. It is 18,754 bp long, consists of nine exons and eight introns and encodes a 493-amino acid long protein. This gene shows six restriction fragment length polymorphisms, of which the RsaI polymorphism (CYP2E1*5B; C-1054T substitution) is of special interest. PCR amplification gives a 413 bp fragment which is wild type. RsaI digestion of this amplicon gives rise to two distinct band due to presence of Rsa I/ Pst I recognition site. RsaI digestion of the amplified region produces bands of 360 and 53 bp. These three different variety are known as c1c1 (wild type undigested by RsaI), c1c2 and c2c2 (digested by RsaI). In our study population the frequency of c1c1 allele is 49% in group I, 67% in group II and 63% in group III (table 2). In group I the median value of total urinary arsenic concentration is significantly lower (p<0.01) in c2c2 polymorphic group than the c1c1 or c1c2 counterpart of the population. In group II also the difference of the median value of total urinary arsenic between c1c1 and c2c2 group is significant. The occurrence of arsenic induced skin manifestation is greater in c2c2 genotypic variation of CYP2E polymorphism though not at a significant level in group I.

4. Discussion:

CYP450 are phase I enzymes responsible for activating most environmental pre-carcinogens, whereas glutathione S-transferases (GSTs) are phase II enzymes capable of detoxifying the electrophilic carcinogens that result from the action of CYP enzymes.

CYP and GST enzymes are highly polymorphic with some of these polymorphisms affecting enzyme expression and/or activity. Functional alteration due to genetic polymorphisms of these enzymes thought to be linked with genotoxic effects as well as overall clinical manifestations of xenobiotics [25,27, 22].

A positive association has been identified between the genetic polymorphism of CYP 450 and the susceptibility to lung cancer in persons having cigarette smoke (Song et al 2001). Similar positive association has been identified between the polymorphic variation of GSTMITI and lung cancer in persons taking tobacco [25]. In Indian population a high risk group of colorectal adenoma has been identified having smoking habit. Homozygosity for the CYP IAI MspI mutant genotype (CYPIAI T-C) is positively associated with in situ colorectal cancer in Japanese (P =0.008) and Hawaiians (P < 0.001). A similar association was identified in the same gene for exon 7 mutational homozygosity in Japanese [24]. Association between CYPIAI gene polymorphism and occurrence of emphysmatic damage to the lung parenchyma has been detected [28].

Our study is a cross sectional study in the population of West Bengal suffering from chronic arsenic exposure through their food. We observed that there is differential degree of clinical manifestations in people receiving same concentration of arsenic through their food and water. We are therefore evaluating the role of xenobiotic metabolizing enzyme and their polymorphisms in differential expression of clinical manifestations coming from chronic arsenic exposure.

Liu and coworkers showed that arsenic increases the expression of GSTM1, GST T1 and glutathione reductase in tumorous and non tumorous liver tissue when administered orally in adult mice [29]. A reduction of hepatic GSH level has been found to greatly decrease the urinary level of MMA and DMA in experimental animals. Low level of GST activity might decrease the level of reduced glutathione therefore, persons having null genotype of GSTM1 or GSTT1 may have altered arsenic methylation capacity and therefore may have a chance to increase the retention of arsenic in the body in comparison to persons having non-null genotype. This hypothesis has been tested on arsenic exposed residents of Taiwan [30]. In exposed population, null genotype of GSTM1 was associated with increased percentage of inorganic arsenic in urine and the null genotype of GSTT1 was associated with increased percentage of DMA in urine [30]. These findings indicated that GSTM1 can facilitate the methylation of inorganic arsenic and therefore may determine the concentration of inorganic arsenic which is retained by the body. We have not done the speciation of urinary arsenic in this study. In our population people having GST M1 and GSTT1 null genotype (M-T+ or M+T-) and base substitutions in CYP1A1 polymorphism are associated with an increase in arsenic induced skin manifestations measured as clinical symptom score.

In continuation, it has been reported also that the distribution of c2/c2 genotype of CYP2E1, detected by PstI or RsaI digestion, differed significantly between gastric carcinoma patients and controls [31,32]. Literature review reveals that in a Chinese population that GSTM1 null genotype, independently or in combined with at least one Val allele of CYP1A1(i.e, A+G+ or A-G+) might affect the genetic susceptibility to lung carcinoma. Individuals with GSTM1 null, and the combined GSTM1 null/CYP1A1 (Ile/Val) or GSTM1 null/CYP1A1 Val/Val had an elevated risk of lung carcinoma [33, 27]. Further, Adonis and coworkers showed that

GST and CYP gene polymorphism have an association with lung resulted from chronic arsenic exposure [34].

In Indian populations we have studied the risk of arsenic induced skin manifestations which is found to be significantly higher in persons having GSTMI or GSTTI null genotype. Whereas, the frequency of occurrence of GSTMITI null (GSTM-T-) genotypic variety in the study population was very low. Therefore it is impossible for us to determine the risk factor of arsenic induced skin manifestations associated with GSTMITI null (GSTM-T-) genotype in reliable quantitative terms. The persons having A+G- genotype may be represented as a high risk group for developing arsenic induced skin manifestations as the body retention of arsenic is apparently much higher in this group than the A+G+ and than A-G+ group. Presence of Ile/Val might be affecting the detoxification/metabolism of inorganic arsenic and thereby decrease body retention of arsenic. In group I, person with GST MI null with combination to A+G- genotypic variation has been associated with an increased risk of arsenic induced skin manifestations. This is probably due to increased body retention of arsenic.

However, there was no association between the CYP IAI (T-C) polymorphic variation and occurrence of arsenic induced skin manifestations and total urinary arsenic in our population. Arsenic inhibit the induction of CYP IAI gene by 2, 3, 7, 8 TCDD [35]. Acute exposure to arsenite decreases the induction of CYP1A1/2 proteins and activities in cultured human hepatocytes, and alters induction of CYP3A23 in cultured rat hepatocytes [36]. We have not found any association between arsenic induced skin manifestations and GST MITI or CYP 450 polymorphism in group II. We propose that, this may be due to the specific frequency of occurrence of GSTMI and GSTTI null allele CYP IAI , CYP T-C and CYP 2E polymorphism and their combination in our study population. The frequency of occurrence of GSTMI or TI null allele and CYP IAI A-G wild type is much lower in group II in comparison to group I (p<0.05).

This low frequency of occurrence may play a protective role in the development of arsenic induced skin manifestations in this group despite high concentration of arsenic in their drinking water. Moreover, in this group the frequency of occurrence of GSTMI null and CYPA+G- in combination is very low. Comparison between group II and III in respect to the occurrence of GSTMI null allele and CYP A+G- allele alone and in combination have failed to show any significant differences.

In conclusion, our present findings have shown an association of the wild type homozygous polymorphism of the CYPIAI gene exon 7 and GSTMI & TI null allele, both individually, and in combination, with arsenic induced skin manifestations, in chronic arsenic exposed population. Apparently, this constitutes a fairly high risk group of arsenicosis. Occurrence of c2c2 polymorphic variety is high in Group I than in group II which constitute a high risk group of arsenicosis. However, the data does not show any correlation of polymorphism with the age, sex and occupational status of the exposed population. In our future studies we will look into the combined etiological roles of smoking, nutritional and dietary status vis-à-vis the methylation profile of arsenic within arsenic exposed population to identify other risk factors.

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Next Generation Rainwater Harvesters and Smart Ground Water Replenishment

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Abstract

India being a subtropical peninsula receives a lot of rain almost throughout the country. In India generally there are sheds fixed over houses in India and the water is either directed and passed through either the gardens or directly into the drain. This leads to a excessive wastage of water, that too rainwater, one of the purest form of water. Our research primarily focuses on upgrading pre-existing sheds implementing rainwater harvesting methods in a manner that it becomes more effective and economical for people of all classes. We have developed designs for harvesters keeping in mind the climate, installation parameters and financial aspect of the common people, especially those in remote locations. The concept of ground reservoirs are generally new, with many people implementing and installing under-ground water tanks. But the concept of refilling the underground water reservoirs deep in the earth is generally missing from those ideas. Apart from rainwater harvesting, we have also focused on refilling groundwater with the excess waters collected and not in use. The ground water being the primary source of water consumption in the urban infrastructure is being stressed too much lately, which is resulting in decrease of water levels at an alarming rate. Our goal is to take a small step in managing the current water crisis that befalls our generation. Our project dealt with the practical usage of the proposed models and whether they meet the target to surpass pre-existing models on terms of efficiency and economy.

Keywords: Rainwater, Harvesting, water, ground water, reservoir

Introduction

Inefficiency in water storage, replenishment and lack of enthusiasm in methodical water consumption has led to this day of scarcity of ground water. Drinking water unavailability has made people migrate from their location and has let the government spent millions in projects to transport water to the water deprived cities from the nearest water purification facilities and nearby states. Thus, there is a need for the citizens to take the matter in their own hands and start small by installing water harvesters in their homes, apartments, offices which shall lead to saving water for multipurpose use and further to replenish and recover the groundwater levels to its former state.

Among the many UN millennium development goals, one of them is to reduce the population of the people without sustainable access to safe drinking water to its half. Another of their goal is to reduce the population of the proportion of the people to half who suffer from undernourishment and hunger. Still around a billion of people do not have access to safe drinking water and about 840 million people suffer from malnutrition. [1]

Most of the Nations which are classified as water – scarce countries, having very low erratic rainfall, resulting in risks of high drought, frequent food insecurities [2] and intra seasonal dry spells. The ratio of rainfall to evaporation is highly unsatisfactory.[2,3,4] The rainfall varies from 200- 600 mm when comparing arid and semi-arid regions all around the globe. In India, the average rainfall is around 300 - 650 mm which is around 300 - 650 litres per metre square per year. Average rainfall in the Kolkata region is around 1580 mm. Though the average potential evapotranspiration varies from around 1500 and 2300 resulting in poor crops, determining the growth period being in about 2.5 to 4 months in the semi – arid zones.[5]



Figure 1. A Pictographic representation of the various losses of rainwater from the soil. E_S – Soil Evaporations EC– Plant Transpirations R_{OFF} – Surface Runoff D – Deep Percolation R – Total Catchment

Thus, though our main target lies around increasing the catchment but the challenges that lies in front of us are accounting the different water flow components. (Fig 1) Soil evaporations by 30 -50 %, which may exceed the 50 % limit in the sparsely cropped portion of semi-arid regions. Surface runoffs with 10 - 25 %, deep percolation being 10 - 30 % of the rainfall [5] occurring in the area. Plant transpiration ranges from 15 - 30 % of the total rainfall merely. Thus, ultimately, around 70 to 85 % of the rainfall is lost from the system as soil evaporation, surface runoff, deep percolations and plant transpirations.(Fig1) Due to the vast increase of the concrete forests around the world the rainwater which used to percolate into the ground, maintaining a sustainable balance between the ground – water level and its usage is failing. It is our aim now to fix the balance to its former state or else due to the imbalance, the tremor activities shall be increasing indefinitely and uncontrollably.

Materials and Methods

TYPES OF RAINWATER HARVESTING TECHNIQUES

Rainwater harvesting is a very long tradition especially here in India. There are many folks found saying "capture rain where it rains" which is thought to have emerged or inspired to practice the culture of Rainwater Harvesting here in India which may have originated in response to the increased aridity in the regions around Indian Peninsula. Thus, these may have contributed to the installations of man made traditional tanks, ponds and earthen embankments to hold and store the necessary water and to allow the excess of it to percolate into the ground

allowing the whole process to move in a cycle. There are around 1.5 million such man – made structures around in India which is still harvesting the water around 660,000 villages around in the country. [6] These encourages the growth of vegetation in the agro ecosystems. [7] In site Rainwater Harvesting – collecting the rainwater where it falls and storing it in thatvery place (in the soil). External Rainwater Harvesting – collecting the Rainwater from a runoff surface at a point and storing it in elsewhere. Both of these practices are used as Agricultural Methods for Rainwater Harvesting. Domestic Rainwater Harvesting – the water is collected from roofs, courtyard and roads. For the urban technological implementations, we shall only focus on the Domestic Rainwater Harvesting.

Agricultural Rainwater Harvesting

In the Indian Peninsula, agriculture is considered as the sole occupation of more than 80% of the population. Rainfed Agriculture is predominant and produces about 90% of the total cereal production of the country. But in many other countries' productivity remains low because of the optimum rainfall characteristics, lack of enthusiasm towards proper water management and unfavorable land conditions. Proper harvest of rainwater should increase productivity, thus increase food security, improve livelihoods and reduce the irrigation frequency that used to be required earlier. [1] For the proper rainwater management there are some primary requirements which should be fulfilled. Most important of them are:

Surface Runoff should be generated immediately duringrainfall. Runoff receiving parmust have soils of suitable texture and property to retain the water and to store it, thus to prevent it from quicklyevaporating. Differences in elevation must be present for the rain to be allowed to flow gradually and get concentrated in the preparedparts. Storage of the water depends upon the run-off collection, land alteration, soil compaction, soil quality and many other textures and features of the soil and its compaction. [5]

Some common systems are – Micro Catchment systems specially designed though slopes and beams to increase the catchment of let it flow directly to the storage area without incurring massive loss. The storage area in here is primarily planting basins in where the plants are to be planted. The soil profile is extremely important in this case because the water available in for the plants are to be protected from evaporation. Thus, micro catchments can be installed using local manpower and materials available. It's comparatively cheaper than the other methods. The three micro – catchments are Contour Bench Terraces, Runoff Strips and Micro Watersheds.Sub surface dams or check dams can be built. Water is stored underground or local sub surface reservoirs which are either made from plastic, cement, clay and different types of compressed soils. They can be built under or above the ground depending on the technological and investment capacity of the investor or the user.

Domestic Rainwater Harvesting

The rainwater collected from the rooftops, streets and courtyards can be stored close and reused for other purposes. This can be achieved through simple mechanisms and storage tanks built under or above the ground depending upon the technology and investments invested by the user. The storage size of the container depends upon the user completely. It is not always strict that a larger tank is always beneficial because the benefit is not always proportional to the storage structure used. Rainwater in the smaller tanks can be easily recycled and emptied often *ISSN* 2689-6389 (Print) *ISSN* 2689-7939 (Online)

whereas in a larger tank complete recycling of the water present in there is improbable. (8) Thus, the costs of the Domestic Rainwater Harvesters directly depend upon the onsite requirements of the equipments needed for the installations. Though the capital costs are high but maintenance and the operational costs are significantly low to none.

Safety provisions of satisfactory enclosure must be kept to minimize the contamination from human, animal or other environmental contaminants. Also, a tight cover must be kept always to prevent algal growth and breeding of mosquitoes, flies and rodents. Open containers such as wells are not recommended for collecting water for the drinking purpose. Smaller tanks made out of bricks, stabilized rammed soil and plastic are common. And for larger tanks concrete, ferrocement or polyethylene are highly recommendable. For increasing the catchment areas through previous usages of sheets as sheds are recommendable, but improving them to some extents might prove beneficiary to the common masses. Some of the designs are Automated-Sunscreens [Mechanical(Hydraulic)], ApartmentHarvesters [Beta 1 – Mechanical(Hydraulic), Beta 2 – Automated (Hydraulicand Motors)], Tanks [Main Tank, Ground Water Refiller, Purifier] and Building Wall Water Collector.

AUTOMATED SUNSCREENS



Figure 2 (a)Top View of the Proposed Automated Sunscreens controlled by Hydraulics (b)Side View of the proposed Automated Sunscreens controlled by hydraulics (c)Hydraulic and Hinge Mechanism implementation

Instead of the old, conservative ways of concrete sunscreens we have theorized solar panels with hydraulic automations. The Panels as discussed above earlier has dimensions of $106 \times 3.5 \times 66$ cm. Covering 0.6996 square meteror approx. 0.7 square meter. Thus, if two of these panels are retrofitted in a frame, it can block the water from getting in the windows, it shall also pass those waters to the Building Wall Water Collector or leaf screens fitted along the building at a slant angle till the main discharge pipe, which shall collect the water and directly dispose it off to the water tank at the base of the building.

The panels would be covering an area of 1.4 square meter. Collecting water of about 2213.5344 liters annually. And with an average sunlight of about 2 hrs., shall produce about 200 watts daily.

The energy produced by the solar panel, is to be stored and thus the mechanism will be selfpowered and self-sufficient. (Fig 2)The mechanism shall only be implemented for the topmost floor of the building because the lower floors will not get sufficient sunlight for the project to be viabl

APARTMENT HARVESTERS



Figure 3. One side of the proposed image of the hydraulic apartment harvester with one of the panel up by 22.5 degrees.



0

Figure 4. The image of the proposed hydraulic apartment roof harvester with the panels at 0 fixed with hydraulics at the sides.

The panels of the Apartment Rainwater Harvesters (Fig 3) consist of Hydraulic pillars (Fig5) which support the structure with the panels attached to the frame (Fig 4). The end of the frame shall be attached to a hinge with ball bearings enclosed in aluminium cans.

The frame is to be made out entirely of aluminium to cut down weight and corrosion for the long-term usage. 100-Watt Panels are fixed to each of the single panels. And as the panels shall be retractable with the panel size being $106 \times 3.5 \times 66$ cm. Covering 0.6996 square meter or

approx. 0.7 square meter. The average rainfall in areas of Kolkata – 1582 mm per annum As the panels shall be retractable, when fully extended the panels shall be covering twice as much area provided by a single panel which shall approximate to nearly 0.6996x2 = 1.3992square meter. Thus, the amount of rainwater harvested by a single framed retractable panel will be 2213.5344 litres annually.



Figure 5. Image of the proposed way to support the frame by the hydraulic joint at the end of the frames.

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The amount of electricity provided by the single framed retractable panel when fully extended shall be around 600 Watts a day if the average sunny time be around 3hrs a day. In the summers the sunny time shall be more than the average time and vice – versa in case of winters. Thus, the total production is estimated to range from (400 - 800 Watts)/ day by the single panels.

Excluding the frame and structure costs an average 100-Watt Solar Panel with dimensions as 106 x 3.5 x 66 cm shall cost around Rs. 5K in terms of Indian Rupees. Thus, for a single framed retractable to host two such Solar Panels, shall already have a cost of 10K. (Excluding the cost of the Frame and retraction gears). Thus, for the project to be viable it is recommended to have similar installations in a symmetrical pattern in the opposite side, which shall double the energy output and double the water harvested. A classic PVC pipe slotted along the panels shall be collecting all the water along the way and shall take it down to the Tank at the ground level. The structure has to be supported by Steel or Aluminium pipes from in between the pillars. The symmetrical Hydraulic pillars shall be concerted to a lever and further to an electric mo-

tor for both manual and automatic operations. If the model is symmetrical it shall cover around $1.3992 \times 2 = 2.7984$ square meterof area + the area of the frames and the hydraulic lifts thus rounding it off to around 3.5 square meter. Net power output in a day = 1200 Watts

Water Capturing Capacity shall increase up to 4427.0688 Liters annually. The Automatic Operations shall be handled by Rain Sensors, Wind Sensors, Arduino Uno with Relays connecting the motor for the operation to sustain only in the case of Beta 2 which shall be applicable for the Urban Areas. Similar provisions will be kept for the Beta 1 version of the same model for further modifications.

The whole structure shall be self-powered and shall not need any external energy source to function. Rather the structure will produce excess energy which shall compensate the average requirements for energy in a small household. On an average the roof of house is estimated to have around 800 ftof area i.e. 74.3224 square meter. Cutting down the area for common space,

Water Tanks and Miscellaneous Areas if we still do have an area of 30 square meter, we shall be able to put around 8.57 i.e. 8 such structures with additional area of (0.57 square meter) for hydraulic automation installations. This, shall be a very fruitful economic design to save water, replenish ground water levels and produce electricity all at once. Also, this has to have to go through least maintenance charges as the power will be self-generated and significantly used only when motors are functional for a certain amount of time.



Figure 6. Proposed Panel Frame Design Figure 7. Proposed retraction mechanisms for the upper panel.

It shall be used to move the panel to and fro through a channel which shall be fit onto the frame. Also, during high currents or violent storms the frames shall retract (Fig 7) and bend it to lower by 22.5 degrees (Fig 6), thus avoid the structures from getting strained through huge pressures. Also, there shall be failsafe levers which shall always be to implement by shutting down the circuits and pulling down the lever. The opposite frame to the side facing sun, would

have gone up by 22.5 degrees. Thus, the panel shall always face the sun directly, for maximum energy production. For that purpose, the hydraulics have to be raised after 3 hours a day.

Hydraulics will primarily be controlled by motors, pressure controlling valves and a pressure release valve as a Failsafe Measure. The hydraulics shall automatically retract and pull down all the frames in case of any faults which shall be the safest case in any probable situations.

The water flow has been shown through the arrows. In case of cost cutting, B and F may be used commonly, minimising maintenance, saving space. But before the water enters B from A, a First Flush Water Diverter must be present. Main Tank is to store and collect all the rainwater falling through the catchment area. One of the pipes shall lead the water to a smaller tank which shall hold the mechanisms to purify the water for drinking and for its usage in other domestic purposes. The mechanisms which are to be applied are discussed below in the Quality and Treatment subsection. Also, an overhead overflow pipe will lead to the Ground water replenisher which shall pass all the excess water which the tank cannot store to recharge the Ground Water levels.

The tank can be placed on the roof or on the ground. If the tank is placed on the ground then a pump will be needed to be used to pump necessary water to the purifier and the common water tanks on the roof. It is to be noted that before the water reaches from the catchment area to the Main Tank, it is to go through a First Flush Water Diverter and a Quick Sand Filter. This reduces the tank cleaning and maintenance charges.

TANKS



Fig 8. Full Proposed Domestic Rainwater Harvester Design A – Catchment Area B – Intermediary tank C – Purifier D–MainTank E – Ground Water Refiller F – Common Tank

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Ground water replenisher shall be a symmetrical cuboidal container where the excess water from the reservoir shall be dumped into. The container is advised to be made out of aluminium to avoid corrosion. Iron or it's alloys, if used, will rust away with time. The base of the reservoir will have fine sand and underneath it the earth. Thus, there shall be no solid sections underneath. Excess or unused water shall be dumped in here, where by the natural process, shall seep into the earth and recharge ground water.

The top of the reservoir shall be completely sealed and have a manhole to access. But precaution must be kept that the lid must be kept closed to avoid algal growth and breeding of mosquitoes and rodents. There shall also be an overflow pipe in case of any gases formed inside to pass out.Purifier shall be a smaller tank preferably made out of plastic or food grade polymers. It is the tank where all the purified water shall be stored in. The purifying and treatment mechanisms are discussed in the Treatment Section.

BUILDING WALL WATER COLLECTOR



Figure 9. Proposed Building Water Collector Above : Sideview Below : Top View These are leaf screens attached to the buildings with an angle of 1 degree to 2 degree

Building Wall Water Collector (Fig 9) are thin metal structures such as 1 inch to 2 inch leaf screens which shall be fixed throughout the building in a slant angle of 1 to 2 degrees. Thus, all the water falling from the walls of the building will be collected and shall be directed to the base storage tanks. These methods if applied can save gallons of waters throughout the year and shall cost no further maintenance charges.

RAIN-WATER HARVESTER PODS (RWH PODS)

Rain barrels and rain catchers have been used for decades but the primary problem lies in their storage capacity and the surface area of the rain-trap. We have designed a pod, bioengineered from the natural shape of a lotus. The pod is pear shaped and has two layers, each having the capability to open up and shut tight, controlled by a small gear mechanism at the base of the pod. The outer pod is made of plastic and it has an inverted umbrella like structure, able to cov-

er thrice the area when open, thus trapping more rainwater. The inner pod is a metal capsule having concave petal like structures which open up to form a mini solar tower. A rod emanates from the centre of the inner pod, and the design is such that it converts sunlight to electricity by heating air (due to focused sunbeams) and rotating turbines.

The whole pod is designed in such a way that it can function in both sunny and rainy days. The pod can be controlled either manually or by IOT using Arduino which reads local weather data and chooses which pod is to function. The base of the pod is made in such a way that it can retract when pod is inactive. Thus, the whole hidden rod inside the pod can also do the same, giving the pod a huge number of capabilities to customise itself according to the situation. This is achieved by using a combination of compliant mechanism^[13] and origami^[14].

QUALITY AND TREATMENT

Quality of the Collected Rainwater

The quality of the rainwater depends vastly on the location of the Rainwater Harvesting System. If the RWHS is located near or in a village, then it is hoped to be clean except for the presence of some of the dissolved unwanted atmospheric gases. But if the RWHS is near or in a city then the quality of the water worsens due to some factors. Atmospheric Pollutants including particles, SPMs, microorganisms, heavy metals and organic substances washed out from the atmosphere, high traffic and Industrial impacts and emissions, catchment surface may themselves be a source of heavy metal and organic substances. Catchment surfaces are suggested to be made out of tiles, slates and aluminium sheets. The surfaces should not be made out of organic substances like roofs tied out of bamboo gutters, as they are to be considered as least suitable because of possible health hazards and safety violations. Zinc, Copper and other heavy metal coatings over the catchment areas are also not suitable because of high heavy metal concentrations in the water which shall be harmful for the body.

Rainwater components naturally match the WHO's criteria for the drinking water standards generally. But if the catchment area is near busy roads or industrial areas, then the rainwater may be polluted from brakes, tires, organic components like polycyclic aromatic hydrocarbons and aliphatic hydrocarbons from incomplete combustion processes. Bacterial, Virus and Protozoal contamination may originate from the feces of birds, mammals, animals, reptiles over the catchment area or the storage tanks. It has been found out by a research conducted by Sazakali analysing three widely used bacterial indicators that there are presence of coliform in 80.3% of rainwater samples, Escherichia coli and Enterococci in 40.9% and 28.8% respectively. (9) For making this water attain the drinking water standards the water has to go through removal of these compounds and disinfection must be carried out to improve the microbiological quality of the water.



Figure 10. Inner and outer pod of RWH

Results and Discussion

Treatment of the Harvested Rainwater

Atmospheric pollutants including particles, heavy metals, microorganisms and organic substances, accumulate on the catchment areas as dry deposition and are washed away and gets mixed with the first rain in the storage vessels and contaminates the water at a whole.

Disinfection include chlorination, ozonization, Ultra-Violet (UV) Filters and Membrane Filtration. Coliform bacteria presence is to be eradicated if the drinking water is to be made potable.



Figure 10. Pictographic representation of Flush Water Diverter The outlet from the slow release valve may be used to perform drip irrigation for plantations in a small area. To remove larger materials from getting inserted into the stream leaf screens are used at the sheditself.



Figure 11. Pictographic representation of the Slow Sand Filters

For treatment of water in developing countries, they mostly aim to treat the water at inexpensive method. Thus, the primary step of rainwater treatment is to pass the outflow channel through first flush water diverters (Fig 10). First Flush water Diverters are a simple mechanism which separates the water flowing at the beginning of the rain, which contains the maximum of the contaminants and then drains it out so that it does not mix with the remaining water stored in the storage tanks. They are easy to install, cheap, operate automatically and available in different sizes for different suitable requirements, thus improving the quality of the rain as well as reducing the tank maintenance.Slow Sand filters (Fig 11) are another inexpensive method to filter out and improve the bacteriological quality of the water. [11][12]

The filters work on biological treatment rather than the conservative process of physical filtration processes. The filters are made of carefully constructed graded sand layers, from the coarsest to the finest to the way down. The slow sand filtration system may last for several weeks to months and are already in effect in many of the developing countries. It provides suitable drinking water standards which many physical processes cannot achieve so easily. Since the nutrient contents remain low in the water, it can only reduce microorganisms but not eliminate them completely.

Chlorination is the next step which is comparatively inexpensive to the other methods and can be applied for the elimination of other microorganisms. Chlorination is to be applied after the water is taken out of the storage tanks, in many cases the chlorine may react with the sediments in the storage tanks and create undesirable by-products which may not be suitable for drinking. (10) The chlorination should be done in an amount of 0.4-0.5 mg/L quantity and can be done by chlorine tablets or gas. The limitation of this process is that some parasitic species showed resistance to lower dosage of chlorines applied in the procedures. Another method to treat the water is to apply the pasteurisation process through solar heaters to cheaply disinfect the rainwater. It is achieved by combining the UV-A radiation with heat. Though this has to be a time taking process, where the water is kept in transparent bottles or jars and maximum amount of sunlight is passed through it, either naturally or by putting multiple reflective sur

faces around it to concentrate the sun rays as a single position. This method is being used in *ISSN* 2689-6389 (Print) *ISSN* 2687-7939 (Online)

many developing nations and it proves to be a successful cheap water treatment procedure.Membrane filtrations like Reverse Osmosis should be applied to remove Radium, Natural Organics, Pesticides, Cysts, Bacteria and Viruses.

Pressure driven membrane technologies include micro-filtration, ultrafiltration, nano-filtration and Reverse Osmosis.





These processes are costly. And is to be used to make the water potable.

UV installations (Fig 12) are not always compulsory. But if we apply UV directly to the unfiltered water, without letting it pass through filtration systems, the micro-organisms, hiding in the shadows of bigger particles, shall be able to pass through unaffected.Further, this water has to be stored in as secure clean container which can protect it (the water) from the physical and chemical effects of the container. Thus, metals should be primarily avoided and in case of this, plastic or fibre storage unit shall be ideal.All the equipment needs to be cleaned, maintained and changed as per requirements.

Conclusion

Everyday, the demand for drinkable water increases due to population growth and expansion in urbanisation and irrigated agriculture. In order to cope up with this dire situation, adopting rainwater harvesting on a wider scale is necessary. Rainwater quality exceeds surface water quality but much of it goes to waste due to lack of proper rainwater harvesting facilities. The ones in existence are inefficient and costly, thus failing to be used as an alternative. We have tried out several alterations of the previous models. Eventually, we improved the mechanics of the system by adjusting several key factors like the folding mechanism on solar panels and blooming mechanism of RWH pods. We brought down the cost a little by making the devices compatible with low-cost building materials like recycled raincoats, which could be used to make the pods. The mechanisms need to be tested out on a broader field over several parameters to make sure they work fine under most situations, like heavy rainfall and storms.

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Accumulation and potential health risk of arsenic in common vegetables grown incontaminated sites of Murshidabad district, West Bengal

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Abstract

There is a growing concern about food safety and environmental contamination due to potential health risk of consumers. An investigation was conducted to study the arsenic accumulation in locally grown vegetables, soil, water at Domkal and Beldanga block of Murshidabad district and also evaluate the possible health hazard to the inhabitants from intake of arsenic contaminated vegetables. Irrigation practices of those areas mainly depend on ground water. From the result it is found average arsenic concentration ranging from 0.18 to 0.49 mg L⁻¹. The arsenic contaminated ground water is used extensively for crop irrigation in Murshidabad district as well as West Bengal. So the arsenic contamination in agricultural soil and agronomic products may be expected. A result revealed that range of mean arsenic concentration is 1.4-6.9 mg kg⁻¹. From the study, arsenic contents of both leafy and non leafy vegetables varied significantly. Maximum mean arsenic concentration in investigated vegetables from the area are 0.05mg kg⁻¹(hyacinth bean), 0.06mg kg⁻¹(onion) and 0.04 mg kg⁻¹(bittergourd), 0.05mg kg⁻¹(lady's finger) respectively. The estimated daily intake ranged from 0.10 to 0.23 mgkg⁻¹body weight for adults. The target hazard quotient calculated was greater than 1; the highest values were 52 for the post monsoon and 55 for the pre monsoon season, indicating the risk of carcinogenicity by consumption of arsenic contaminated food.

Key Words: Vegetables, Arsenic accumulation, Daily intake, Hazard quotient, Murshidabad.

Introduction

Arsenic (As) poses a severe threat to human health through exposure pathways mainly including water and diet. The first report of groundwater As contamination and its health effects on people living in the Ganga plain of West Bengal was published in 1984.[1]. Under certain geochemical condition, As can be mobilized from soil to ground water.[2,3]. The epidemiological study established a report on carcinogenic effect of As on humans and have related the element with numerous other skin diseases [4,5].

The methodology for estimation of target hazard quotient (THQ) indicates the ratio of the

potential exposure to a substance and the level at which no adverse effects are expected. If the hazard quotient (HQ) is calculated to be less than 1, then no adverse health effects are expected as a result of exposure. If the HQ is greater than 1, then adverse health effects are possible. Based on the previous reports of Roychowdhury et al.(2002) [6], studying over the As affected area of Murshidabad, West Bengal, it was found As accumulation in various food composites like (potato skin, leaves of vegetables, rice, wheat, cumin, turmeric powder, and cereals) ranged between <0.0004 and 0.693 mg kg⁻¹. Vegetable is an important part of human diet after rice, so for most of the people it is also the main route of exposure to toxic element through dietary intake. The food crops grown using arsenic contaminated water are sold off to other places, including uncontaminated regions where the inhabitants may consume arsenic from the contaminated food. A number of studies were carried out in As affected areas of Bengal delta plain [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22].

The objectives of the present study are: (1) to determine the accumulation of arsenic concentration in water-soil-vegetables at two studied location of Murshidabad district throughout the year (2) Estimation of the daily intake through consumption of these contaminated food (3) to evaluate the potential risk of arsenic from contaminated vegetable consumption to human health through THQ.

2. Materials and Methods

2.1 Sampling location

Two blocks, namely, Beldanga (latitude 24 ° 50′ N, longitude 88° 46′E) and Domkal (latitude 23° 43′ N, longitude 87° 49′ E) of Murshidabad district have been chosen for the present study. In these areas the level of arsenic in groundwater exceeds the permissible limit for drinking water of 0.01 mg L^{-1} [23] and the permissible limit for irrigation water of 0.10 mg L^{-1} [24].

2.2 Vegetable, Water, soil sampling

The vegetable samples were collected seasonally (premonsoon, monsoon, postmonsoon) from this area. Groundwater samples have been collected from shallow tube well pumps with large diameter in 100mL bottles with 3 replicates, and preserved with 1mL L^{-1} concentrated HNO₃. Surface soil samples were collected from 0-10 cm depth and sub-surface soil samples were collected from 10-50cm depth by composite sampling from the fields and transferred it to into air-tight polythene bags.

2.3 Sample Treatment

Plant samples were washed thoroughly with tap water followed by de-ionised water for several times. Finally the samples were dried in hot air oven at 50°-60°c for 72h, powdered and stored in air tight polythene bags at room temperature. Water samples were filtered through 0.45 μ Millipore filter paper and the filtered samples kept in polythene bottles at 4°c prior to analysis. The soil samples were immediately sun-dried after collection and later dried in hot air oven at 60°c for 72h, grinded and screened. Finally the samples were stored in air tight polythene bags at room temperature.

2.4 Sample Digestion

Vegetables and soil samples were digested separately following heating block digestion procedure.[25]. Plant samples were digested by adding perchloric acid (HClO₄), sulphuric acid (H₂SO₄) and nitric acid (HNO₃) at 1:1.5:4 ml ratio. The tubes were placed on a heating

block at 110° - 120° c until a clear solution was obtained. The samples were cooled, diluted to 25ml with de-ionized water and filtered with Whatman No. 41 filter paper. For soil sample, concentrated H₂SO₄ was added in addition to concentrated HClO₄ at 3ml: 2ml ratio. Then the tubes were heated at 160°C for about 4-5h. The heating was stopped when the dense white fume of HClO₄ was emitted. The content was then cooled, diluted to 25ml with de-ionized water, and filtered through Whatman No. 42 filter paper.

2.5 Analysis of total arsenic

The total arsenic of samples were analyzed by flow injection hydride generation atomic absorption spectrophotometer (FI-HG-AAS, Perkin Elmer AAnalyst 400) using external calibration. [26]. The optimum HCl concentration was 10% v/v and 0.4% NaBH₄ produced the maximum sensitivity. Standard reference materials (SRM) from National Institute of Standards and Technology (NIST), USA, were analyzed in the same procedure at the start, during, and at the end of the measurements to ensure continued accuracy.

2.6 Data analysis

Estimated Daily Intake of arsenic from vegetables: Estimated daily intake (EDI) ($\mu g/(kg body weight (bw/d))$ of arsenic from vegetable consumption was obtained by Eq. (1):

$EDI = (C X F_{IR}) / W_{AB}$

where, C (µg/g fw) is an average weighted arsenic content in the edible portion of the vegetable, and is calculated by multiplying the mean arsenic content in vegetables with their corresponding percentage of consumption. F_{IR} (g/d/person) is a daily vegetable consumption.[27].

Health Risk Assessment

Health risk is associated through As contaminated vegetables consumption based on the ratio between the exposure and reference dose (RfD) and is used to express the risk of non-carcinogenic effects and were assessed using Target Hazardous Quotient (THQ) [28,29,30,31]. This method is available in US EPA Region III Risk-based Concentration table [30] and it is described by the following equation:

THQ= 10^{-3} (EF x ED x FIR x C/RFD x WAB x TA)

(2)

(1)

Where EF is the exposure frequency (365 days/yr), ED is the exposure duration (70yrs), FIR is the food ingestion rate (g/person/day), C is the concentration of food, RFD is the oral reference dose; As = $3 \times 10^{-4} \text{ mg/kg/day}$, [29], WAB is the average body weight (60kg), TA is the average exposure time for non-carcinogens (365 days/ year X number of exposure years, assuming 70 yrs in this study).

3. Result and discussion

3.1 Arsenic concentration in irrigation water and soil

Agriculture is the most important livelihood in the study area and is in practice throughout the year using groundwater as the main source for irrigation. Shallow tube well pumps are used for irrigation in this area (running 8h-10h per day). From this study, mean arsenic concentration of water sample ranged from 0.28-0.38 mg lt⁻¹ in Domkal and 0.25 - 0.44 mg lt⁻¹ in Beldanga, which is many fold higher than WHO/FAO permissible limit. (Table 2 and

Figure 2). The heavy withdrawal of ground water may be the reason of iron pyrite decomposition and release of arsenic in water. [31,32].

The total arsenic concentration in investigated soil ranged from $2.85 - 6.8 \text{ mg kg}^{-1}$ in Domkal and $2.54 - 4.09 \text{ mg kg}^{-1}$ Beldanga (Table 2 and Figure 2). Previously it has been said that arsenic accumulation in soil is due to irrigate with arsenic-contaminated ground water in West Bengal [33,34]. Thus the results clearly showed that extensive use of arsenic-contaminated ground water in the study site for irrigation may increase level of arsenic in soil. The highest content of arsenic in soil was reported (19.4 mg kg-1) in West Bengal. [35]. The accumulation of arsenic in soil of the study area was lower than the reported global average of 10.0 mg kg⁻¹[36] and was below the maximum acceptable limit for agricultural soil of 20.0 mg kg⁻¹, recommended by the European Community[25]. Thus there is a possibility of increasing arsenic concentration in soil in future if the trend of ground water irrigation will not restricted

3.2 Uptake of arsenic by vegetables

To monitor total arsenic content, collected vegetables with replica were analyzed for the present study. (Table 1 and Figure 1 near here). Table 1 describes the mean arsenic content in different collected vegetables where it is ranged from 0.048-0.34 mg kg-1 i.e, Hyacinth Bean and Potato respectively. Das et al. (2004) [37], from their study in Bangladesh, also found higher arsenic contents in potatoes (0.07–1.36 mg kg-1). But, very low arsenic accumulation in potato (<0.01 mg kg-1) was reported from a study in Nepal. Food composites (potato skin, leaves of vegetables, rice, wheat, cumin, turmeric powder, and cereals, etc.) collected from As-affected areas of the Murshidabad district, West Bengal, contained 7–373 μ g kg⁻¹asenic [6].The uptake of arsenic by agricultural plants depend on water requirement, soil properties[38,14]. Previously it was predicted that the higher concentrations of arsenic was found in potato, arum, amaranth, radish, lady's finger, cauliflower, brinjal, etc., is due to irrigated with arsenic contaminated water [39,40,6]. Thus the arsenic content in the analyzedsample of the study area is more or less equivalent comparing with the reported value of cultivated vegetables of Nadia district.

3.3 Food habit and arsenic intake of local habitat

Rice and vegetables are the main staple food among the local people of the study area. After learning the arsenic rich exposure from food and drinking water, we have studied arsenic in vegetables. After surveying randomly 30-40 family, it has been found that, normally people of those areas eat rice, vegetables and dal three times per day (Table 3 near here). Adult (both male and female) normally eat 150gm of rice with 100gm of vegetables in morning and 250gm of rice at lunch and dinner with around 200gm and 150 gm of vegetables at each meal. The average vegetable taken by adults are 450 gm respectively i.e. 90gms in dry weight (about 80% moisture content in vegetables).

3.4 Estimated daily intake (EDI) and Target Hazardous quotient (THQ) of arsenic from vegetables consumption:

Estimated daily intake (EDI) and target hazardous quotient (THQ) of arsenic were calculated for local people considering the average concentration of arsenic through consumption of vegetables (Table 4and Figure 3 near here). Comparing the EDI value of three season, higher

intake value was found in post monsoon, i.e, 0.223 mg/(kgbw/d) in Domkal block and 0.23 mg/(kgbw/d) for pre monsoon in Beldanga block for adult age group. Incase of Domkal block

the EDI value for pre monsoon and monsoon was 0.178 mg/(kgbw/d) and 0.145 mg/(kgbw/d) whereas in Beldanga block the value was 0.102 mg/(kgbw/d) and 0.148 mg/(kgbw/d) for monsoon and post monsoon. Thus the As intake from vegetable was lower than 0.463 μ g/(kg bw/d) that for adults in Bangladesh[39,42] and higher than 0.174 μ g/(kg bw/d) for adults in West Bengal , India [8]. Based on toxicological evaluation of suggested the provisional daily intake (PTDI) for inorganic arsenic was 2.1 μ g/(kg bw/d) or (0.0021 mg/ kg body wt. per day). Considering the seasonal consumption of As through vegetables, it can be say that vegetables which grown in post monsoon and pre monsoon of the studied region, might be cause more risk for human health comparing two other season.

Blocks	No. of samples	Variety in pre	Arsenic concentrat	Variety in	Arsenic concentrat	Variety in post	Arsenic concentration	Mean arsenic	Mean arsenic
		monsoo	ion in	monso	ion in	monsoon	in vegetable	concentrat	concentr
		n	(mg kg ⁻¹)	on	(mg kg ⁻¹)	season	$(mg kg^{-1})$	irrigation	ation in
		season	(ing kg)	season	(ing kg)			water (mg	$k\sigma^{-1}$
								L ⁻¹)	ĸg)
Domkal	(n=15)	Beans	0.078±0.	potato	0.23±0.0	vindi	0.077±0.05	0.33±0.0	5.13±0.
24°06.32			05	-	2			5	43
3´´N		Carrot	0.12±0.0	Chilli	0.074±0.	Brinjal	0.072±0.03		
88			3		02	5			
°32.796′′		Potato	0.13±0.0	Seem	0.050±0.	Potato	0.28±0.05		
Е			5		03				
		Brinjal	0.06±0.0	Laal	0.072±0.	Spring	0.21±0.06		
			1	saak	03	onion			
		Spring	0.086±0.	Vindi	0.077±0.	onion	0.063±0.002		
		onion	04		04				
		Onion	0.10 ± 0.0	Bottle	0.075±0.	cabbage	0.17±0.04		
			02	gourd	05				
		Cabba	0.20±0.0	pumpk	0.	cauliflow	0.23±0.03		
		ge	3	in	106 ± 0.01	er			
		caulifl	0.18±0.0			Carrot	0.092±0.03		
		ower	4						
Beldanga	(n=12)	Potato	0.34±0.0	Laal	0.10±0.0	jhinge	0.065±0.05	0.33±0.0	3.51±0.
23°59.15			07	saak	3			4	92
0´´N		Pumpk	0.24±0.0	lau	0.056±0.	seem	0.048±0.04		
88		in	08		008				
°14.389‴		Tomat	0.18±0.0	Biiter	0.037±0.	lau	0.11±0.05		
E		0	07	gourd	03				
		Spinac	0.15 ± 0.0	chilli	0.082±0.	pumkin	0.083±0.002		
		h	3		003				
		Laal	0.085±0.			tomato	0.19±0.04		
		saak	08						
		Bitter	0.053±0.						
		gourd	08						
		Lady's	0.052±0.						
		finger	030						

Table 1- Mean arsenic concentration of Vegetable, Water and Soil samples

4. Conclusion

The results of this study revealed that due to uncertainty of rainfall, most of the area under the two studied block use primarily ground water for irrigation purposes. The ground water

arsenic content was high than the permissible limit proposed by WHO. Analyzing the severity of arsenic toxicity in ground water as well as soil, their uptake capabilities ,which influenced the irrigated vegetables with respect to seasonal variation. A significant As contamination was found in soil as well as irrigated vegetables using As contaminated ground water. Therefore there is a probability of entry of arsenic into the food chain through water soil vegetable pathway. Both the EDI and THQ value from As accumulation were exceed the maximum limit and as a result it may cause health risk to the communities. In conclusion frequent monitoring of arsenic contaminated vegetables grown at the irrigated area is necessary and consumption of contaminated vegetables should be avoided in order to reduce health risk caused by taking contaminated vegetables



Fig. 1 Distribution of Arsenic concentration in vegetable, water and soil samples

Site	Estimated da	ily intake (mg k	g ⁻¹ day ⁻¹) Target hazardous quotient (THQ)))	
	Premonsoon	Monsoon	Post	Premonsoon	Monsoon	Post	
			monsoon			monsoon	
Domkal	0.178	0.145	0.223	41.65	33.95	52.15	
Beldanga	0.23	0.102	0.148	54.95	23.80	34.6	

Table 2- Estimated daily intake (EDI) and Target hazardous quotient (THQ) of arsenic from vegetables



Fig. 2 Comparison between two study site in As concentration of vegetable, EDI and THQ. (range of scale of As conc. and EDI represent 0-0.25 and 0-60 scale range represent THQ value)

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Nanotoxicity in the environment

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Abstract

Nanomaterials have been at the forefront of scientific research for more than a decade. These are microscopic materials. Owing to their higher chemical reactivity and biological activity, many scientists believe that nanoparticles may have a higher risk of toxicity compared to larger particles. Evidence of adverse health effects have been demonstrated invitro studies, in vivo studies, and in epidemiological studies. The rate of production of nanomaterials is increasing thereby widening the field of research. This increases the ability to characterize the potential adverse health risks associated with these materials. Engineered nanomaterials are increasingly produced and utilized in a wide variety of products, and the uncertainties regarding their potential adverse health effects, which are associated with their unique properties, makes risk assessment challenging.Emerging areas of nanotoxicological investigation include the interactions of nanomaterials with other toxicants, either by enhancing, or reducing adverse health risks as well as the potential adverse environmental effects associated with nanomaterials pollution.The growth of the nanomaterials and nanotechnology industries promises many benefits, which should be balanced by effective risk assessment and this is where our interest of research on this topic lies.

Keywords: Nanoparticles, Living organisms, Risk Assessment, SAFER.

Introduction

Nanoparticle (NP) also known as ultrafine particle are defined as the particle of matter that ranges between 1 and 100 nanometres (nm) in diameter. Nanoparticles have unique properties and are highly reactive in nature because they have a greater surface area per weight than larger particle. Nanoparticles are found naturally as well as artificially. Naturally, it is formed during combustion, geological and biological process, and artificially it is formed by the combustion of fuels in automobiles, manufacturing and also from domestic activities like cooking. These nanoparticles have unique physical and chemical properties which have an impact on their toxicity such as: size, shape/structure, surface charge and solubility. Particle sizes range between 1 and 100 nanometres (nm) in diameter. Due to its small size, NPs can easily penetrate cell membranes and other biological barriers into living organisms causing cell damage. Studies reporting increased toxicity of NPs when compared to their

larger bulk particles have led to a generally assumed conjecture that NPs are more potent in causing damage.

NPs are found in different shapes e.g. fibres, rings, tubes, truncated triangles, spheres, and planes. Shape dependent toxicity has been observed for multitude of nanoparticles including carbon nanotubes, silica, allotropies, nickel, gold, and titanium nanomaterials [1].

Surface charge also plays a significant role in toxicity of nanoparticles as it largely determines their interactions with the biological systems. As surface charge plays a major factor in the colloidal behaviour, it specifically influences the organism response upon exposure to nanoparticles by changing their shape and size through aggregate or agglomerate formation [1]. It has been observed that with increase in the concentration of nanoparticles, the toxicity decreases (at higher concentration) [1].

Nanoparticles are apparently solid with a metal bond (metals) or a covalent bond (oxides). Such nanoparticles do not dissolve in organic solvents ethyl alcohol, hydrocarbons dimethylformamide and water. They do not dissolve because they do not receive a gain in Gibbs energy in such a process.When NPs are discarded, they can enter the aquatic environment as aggregates and soluble ions, which can be highly toxic to aquatic organisms. [2,3]

Nanoparticles are being evaluated for use, in many fields. Nano-based technology has made huge progress over the past few decades. The reason for this enormous growth in the production of products containing NPs is their unique general properties (in particular particle size, surface area, surface reactivity, charge, and shape) relative to their bulk or dissolved counterparts. This facilitates a broad range of possible applications. Engineered NP consist of carbon-based and inorganic forms, partly with functionalized surfaces.

We shall now witness the nanotoxicity in the environment, their harmfulness and risk assessment. [4,5,6]

2.Adverse effect of NPs on living organisms

Despite the evident benefits of nanoparticles, it also has negative effects on living organism's health. Due to its quantum size effects (the physics of electron properties in solids with great reductions in particle size) and large surface area to volume ratio. They immediately absorb onto their surface and some of the large molecules encounters as they enter the tissues and fluid of the body. The toxicity of nanoparticles depends upon size, shape and their bulky chemical composition. Many nano-particle have their solubility feature which can easily mix with blood causing breathing problem which may lead to death. Sometimes inhaled nanoparticles lead to great impact on lung inflammation and heart problems.

Some of the element- based nanoparticle have biological effect on the environments like carbon-based nanoparticles (fullerenes, nanotubes), the oxide of metal such as iron and titanium and natural inorganic compound. The elements which having high chemical reactivity and solubility like Na, Ca directly effects the immune system. Human suffers more effect of nanoparticles because it is placed top in the hierarchy. [7]



Figure 1. Biomagnification in the environment

2.1Effects on human health

The human body may be exposed to nanomaterial via a variety of routes, including through Lungs, gastrointestinal tract, skin, nose. Lungs and nose are the most likely way for the NPs to enter easily. The most uncovered part of our body is thnose, through which these particles can easily enter which affect our lungs leading to cardiovascular diseases thereby effecting our blood vessels. There are chances of getting pulmonary disease, respiratory infection and lungs cancer. A structure which acts as the air-blood barrier is present in the lungs that controls the gas exchange(during inflow and outflow of gases through inhalation and exhalation) in the lungs by means of pressure and concentration gradients. However, it can't prohibit the entrance of all other foreign material. In our breathing while inhalation of air we inhale other particles too if they are small enough, for example: bacteria, viruses and also nanomaterials. With nanoparticles being very small in size and the barrier being very thin, the chance for nanoparticles to cross and enter the interior of our body becomes high. Another way of getting affected is through gastro intestinal tract. [9,10]The main function of the gastro-intestinal tract is the uptake of different materials (food), their digestion, and the delivery of the nutrients to the different organs through blood. There is a fair possibility

for nanomaterials to cross the gastro-intestinal tract barrier. However, this only leads to the entrance of a very small quantity of nanomaterials that are considered to be unproblematic but the uptake and movement of large particles may cause Crohn's disease, ulcerative colitis and cancer in gastro intestinal tract.Next is Olfactory mucous membrane, the olfactory mucous membrane is located in the upper part of the nose, called the nasal roof. It is directly connected to our forebrain. NPs when enter here, can cause brain disorders, tumour, etc.[7,11]. Table 1 gives a clear picture of possible risks associated with different nano particles.

NANOMATERIALS	POSSIBLE RISKS				
→Carbon nanomaterials, silica nanoparticle	Pulmonary inflammation, granulomas, and fibrosis [12]				
\rightarrow Carbon, silver and gold nanomaterials	Distribution into other organs including the central nervous system [12]				
\rightarrow Ag NPs	Damage to cell membrane, disrupt ATP, DNA replication, release oxidative ROS [13]				
→ Au NPs	Affects reproduction, in daphnia, mammals, algae, fishes, accumulates in liver, causing oxidative stress [22]				
\rightarrow Quantum dots, carbon and TiO2 nanoparticles	Skin penetration [12]				
\rightarrow MnO2, TiO2, and carbon nanoparticles	May enter brain through nasal epithelium olfactory neurons [12]				
\rightarrow TiO2, Al2O3, carbon black, Co, and Ni nanoparticles	May be more toxic than micron sized particles [12]				
\rightarrow Metal fume (Oxides of Zinc, copper) nanomaterials	Causes metal fume fever, influenza-like reaction.[15]				
\rightarrow Metal dusts (platinum, nickel, chromium, cobalt) nanoparticles	Asthma, lung cancer, sinus [15]				

Table1- Possible risks associated with different nano particles.

2.2 Effect on plants:

The interaction between nanoparticles (NPs) and plants is indispensable. It has both positive as well as negative effects. The positive effects are seed germination in which the rate of germination is more which helps in promoting the growth of some plants like spinach and accelerate nitrogen assimilation. It also helps in increasing productivity and rate of photosynthesis. However, as we know anything in excess lead to negative effects, it inhibits the growth of plants, seed germination, reduces chlorophyll concentration in plants, etc when found in excess. It also spoils the whole metabolism and stages of cell division.[16]

Some organs that get most affected due to nanoparticles are- leaf, root and reproductive system. Leaf being the outermost part of the body of plant is completely exposed to the environment. The landing of particles on the leaves followed by penetration of the stomatal pores take place which inhibits the growth of leaves. Some of the plant species which are roots (like potato, carrot, turnip) get directly affected if they absorb nanoparticle through roots.NPs can disrupt the levels of secreted hormones, causing changes in sexual behaviour. It also reduces the fertility of the plant[17]. The figure(2) here shows the effect of NPs on some of the edible plants[18].

3. Risk Assessment of Nanomaterials

We have already known that due to its small size and high reactivity nanomaterials can be toxic in nature but the fact that nanomaterials have many diverse benefits, makes it the focus point in the field of research. It has immense uses and benefits. It has found its way in the field of cosmetics, textile, electronics and medicines. There arises a need of risk assessment of these nanomaterials to get the best out of them with minimal harm.

As per the research, the major toxicity studies focus on the original form of engineered nanomaterials. Studies suggest that a number of exposure conditions such as the change in the pH level or salinity can bring changes in the physical and chemical properties of these nanomaterials thereby reducing their potential toxicity.

One of the most important points in the assessment of risk of nanotechnology is to distinguish between free nanomaterials and the fixed ones, because of the huge differences in the mobility. Next, we have to distinguish between the nanoparticles formed from technological processes and those that were unintentionally produced and released into the environment by several conventional technologies. Some engineered nanomaterials possibly exhibit critical characteristics when emitted into the environment or taken up by the organ-

isms, therefore the mechanism of transition and potential dermal or systemic toxicity needs to be evaluated[19,20].

Challenges faced in risk assessment:

Some of the major challenges faced in the risk assessment of the nanomaterial are as follows: Firstly, the nature and behaviour of nanomaterials might change during its lifecycle. Also, one of the major threats of risk assessment is that it is yet not known with surety that the changes we bring in the conditions, enhances or reduces the toxicity level. One of the best ways to





find a less hazardous nanoparticle, is designing a less harmful nanoparticle. For this we follow the five principles of designing nanomaterials: **SAFER**[6,21].

4.Conclusion

It is by now a known fact that the nanotoxicity is an enormous field which indicates significant negative impacts on both cellular and larger levels. NPs have different negative impacts depending on its physiochemical properties. Therefore, it may evoke questions in the reader's mind about the increasing rate of production of nano particles. The reason being, after decades of basic nanoscience research and more than fifteen years of focused R&D under the NNI, the significant contribution from the use of nanotechnology to benefit society was exceptional. Therefore, it is no wonder that the growth of these nanomaterials has increased to a lot extend in the last few years. But like there are two sides of a coin it comes along with a lot of harmful effects. This very task of minimalization of toxicity of these hazardous materials without affecting their functionality much, has been a focus-point for many scientists. Therefore, it can be concluded that the study of the five principles and designing of "*safer*" NPs will surely grow in the years to come and we may witness new improved versions of nanomaterials.



Figure 3. SAFER

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Size, Surface,	Alternative	Functionalization	Encapsulation	Reduce the quantity
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such as their	bulk)	the relevant features	particle.	this principle
colour,	to replace the	yet less hazardous in	1	suggests that the use
conductivity,	hazardous one.	nature.		of hazardous
melting-point,				nanoparticle
and other				can be continued, but
physical				in reduced quantity,
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even its				quantity.
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