

### Treatment Methods for Arsenic, Heavy Metals and Fluoride

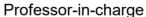
#### Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
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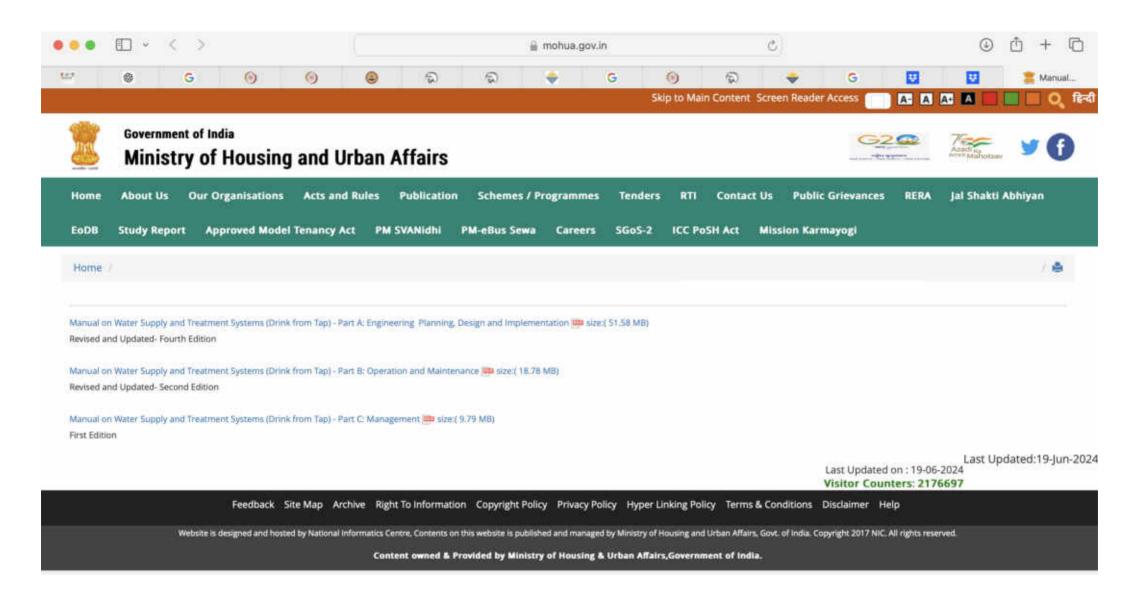




International Centre for Clean Water







https://mohua.gov.in/publication/manual-on-water-supply-and-treatment-systems---drink-from-tap---march-2024.php







## GOVERNMENT OF INDIA MINISTRY OF HOUSING AND URBAN AFFAIRS

# MANUAL ON WATER SUPPLY AND TREATMENT SYSTEMS (DRINK FROM TAP)

PART A: ENGINEERING - PLANNING, DESIGN AND IMPLEMENTATION FOURTH EDITION - REVISED AND UPDATED

### CENTRAL PUBLIC HEALTH AND ENVIRONMENTAL ENGINEERING ORGANISATION

https://mohua.gov.in || https://cpheeo.gov.in



#### WATER RESOURCES

#### Global threat of arsenic in groundwater

Joel Podgorski<sup>1,2</sup>\* and Michael Berg<sup>1,3</sup>\*

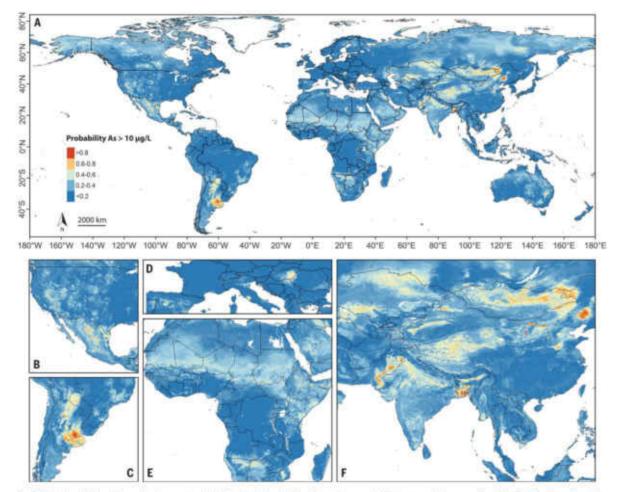


Fig. 2. Global prediction of groundwater arsenic. (A to F) Modeled probability of arsenic concentration in groundwater exceeding 10 mg/liter for the entire globe (A) along with zoomed-in sections of the main more densely populated affected areas (B) to (F). The model is based on the arsenic data points in Fig. 1 and the predictor variables in table S2. Figs. S2 to S8 provide more datailed views of the prediction map.

Using 200,000 data points

Podgorski et al., Science 368, 845-850 (2020) 22 May 2020

Analysis based on machine learning models

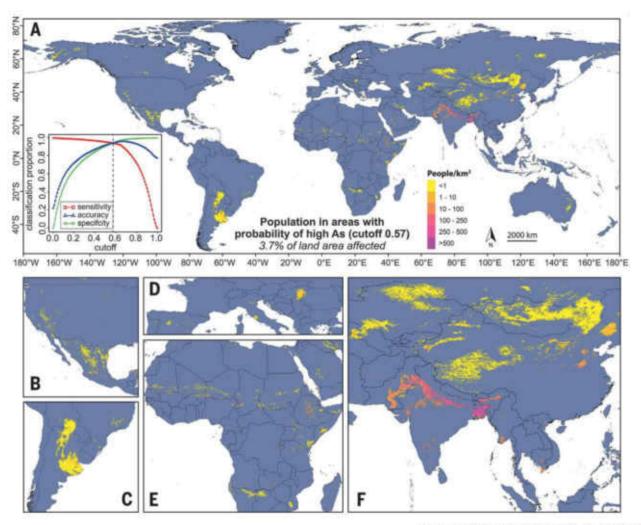
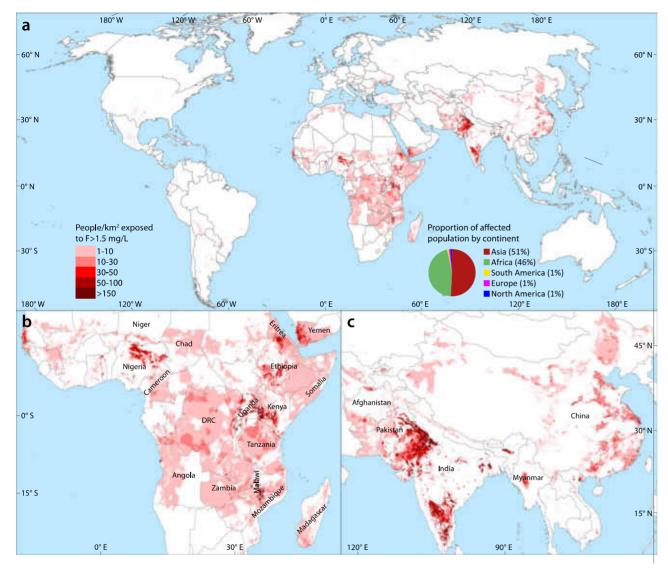


Fig. 4. Estimated population at risk. (A to L) Population in risk areas potentially containing aquifers with arsenic concentrations >10 mg/liter using probability cutoffs of 0.57 (A), at which sensitivity and specificity are equal [inset in (A)] as applied to the full (training and test) dataset, and 0.72 (G), at which PPV and NPV are equal [inset in (G)] using the full dataset. The detailed areas of Fig. 2 are also repeated here for both models (B) to (F) and (H) to (L).



**Fig. 4 Estimated population potentially exposed to fluoride concentrations in drinking water greater than 1.5 mg/L. a** Global map and break-down by continent. Detailed views of **b** sub-Saharan Africa and southern Arabian peninsula and **c** south and east Asia with the most strongly affected countries indicated. The population was calculated with the hybrid approach (see text) for areas with a greater than 25% probability of incurring high fluoride in groundwater (Fig. 1) by multiplying the total population by the hazard percentage and the proportion of domestic water usage coming from untreated groundwater<sup>51</sup>.

ARTICLE

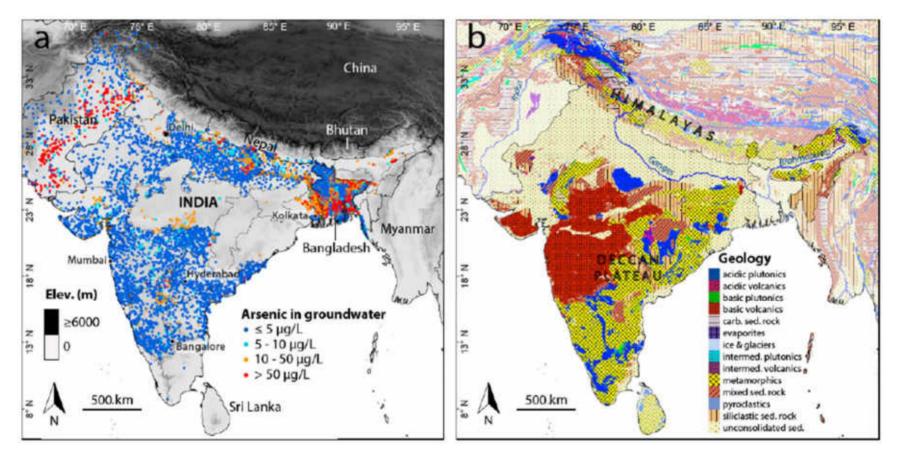
Inthes://doi.org/10.1038/s41467-022-31940-x

OPEN

Global analysis and prediction of fluoride in groundwater

Joel Podgorski 10 182 & Michael Berg 10 188

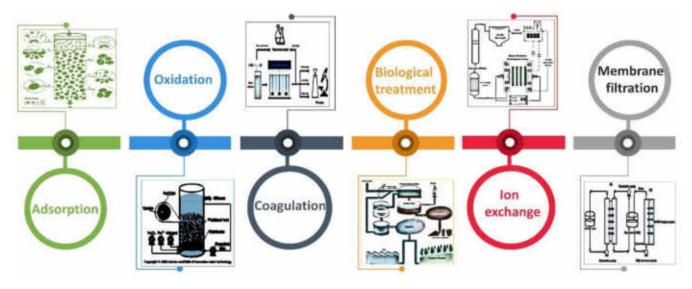
400,000 measurements, 10% > 1.4 mg/L



**Figure 1.** Arsenic concentration in Indian groundwater (a) topographical representation of averaged arsenic data points in Indian groundwater (b) Indian lithology [25].

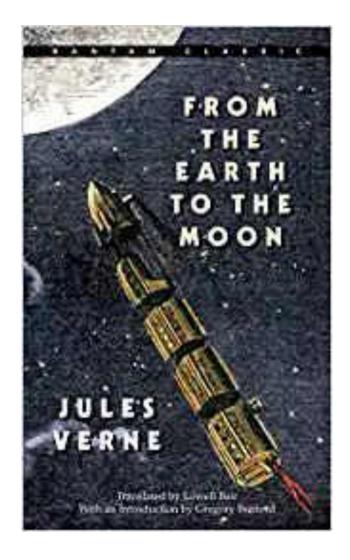
Review

## Arsenic Contamination in Indian Groundwater: From Origin to Mitigation Approaches for a Sustainable Future



**Figure 5.** Various Mitigation Methods for Arsenic Contamination.

Our dreams become reality with materials



### Water purification, history

Important milestones in the history of water purification (1800–2007) from the perspective of noble metal nanoparticles in water treatment (compiled from multiple sources on the World Wide Web).

Year	Milestone				
1804	Setup of world's first city-wide municipal water treatment plant				
	(Scotland, sand-filter technology)				
1810	Discovery of chlorine as a disinfectant (H. Davy)				
1852	Formulation of Metropolis Water Act (England)				
1879	Formulation of Germ Theory (L. Pasteur)				
1902	Use of chlorine as a disinfectant in drinking water supply				
	(calcium hypochlorite, Belgium)				
1906	Use of ozone as a disinfectant (France)				
1908	Use of chlorine as a disinfectant in municipal supply, New Jersey				
1914	Federal regulation of drinking water quality (USPHS)				
1916	Use of UV treatment in municipal supplies				
1935	Discovery of synthetic ion exchange resin (B. A. Adams, E. L. Holmes)				
1948	Nobel Prize to Paul Hermann Muller (insecticidal properties of DDT)				
1959	Discovery of synthetic reverse osmosis membrane				
	(S. Yuster, S. Loeb, S. Sourirajan)				
1962	Silent Spring published, first report on harmful effects of DDT (R. Carson)				
1965	World's first commercial RO plant launched				
1974	Reports on carcinogenic by-products of disinfection with chlorine				
	Formulation of Safe Drinking Water Act (USEPA)				
1975	Development of carbon block for drinking water purification				
1994	Report on use of zerovalent iron for degradation of halogenated organics				
	(R. W. Gillham, S. F. O'Hannesin)				
1997	Report on use of zerovalent iron nanoparticles for degradation of				
	halogenated organics (C-B. Wang, WX. Zhang)				
1998	Drinking Water Directive applied in EU				
2000	Adoption of Millennium Declaration during the UN Millennium Summit				
	(UN Millennium Development Goals)				
2003	Report on use of noble metal nanoparticles for the degradation of pesticides				
	(A.S. Nair, R. T. Tom, T. Pradeep)				
2004	Stockholm Convention, banning the use of persistent organic pollutants				
2007	Launch of noble metal nanoparticle-based domestic water purifier				
	(T. Pradeep, A. S. Nair, Eureka Forbes Limited)				

#### World's first nanochemistry-based water purifier



Our peetode filler is an offshoot of basic research on the chemistry of propertities." Transpol Pladespirits led the learn at IIT Charter told Chartistry. York! He and his student Dreenumeren hair discovered in 2003 that habitarbone such as carbon tetractionise (CCI4) correletely lovest down into metal fullides, and

amurghous person upon reaction with gold and stiver remark/own

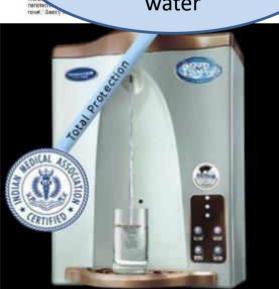
the by runs lively. By research funded by the Department of Science and

Pactivisings in New Delta, his learn found <sup>1,5</sup> that gold and silver remojections paged on assence were meens also to completely remove endoculars, margino

**Chemistry world** 

First ever nanotechnology product for clean water



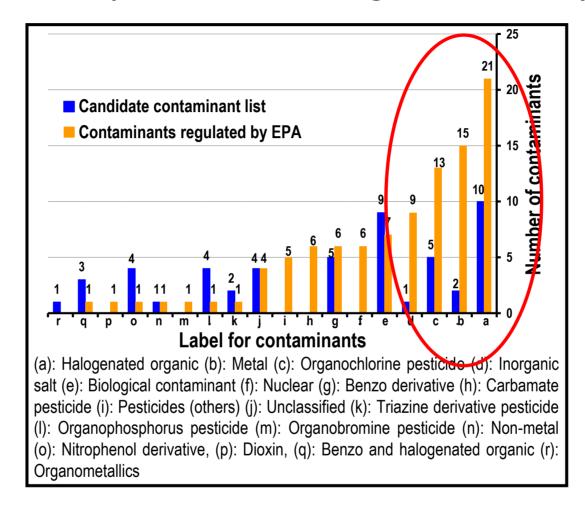




A plant to make supported nanomaterials for water purification; with capacity of 4.5 tons per month, 2007

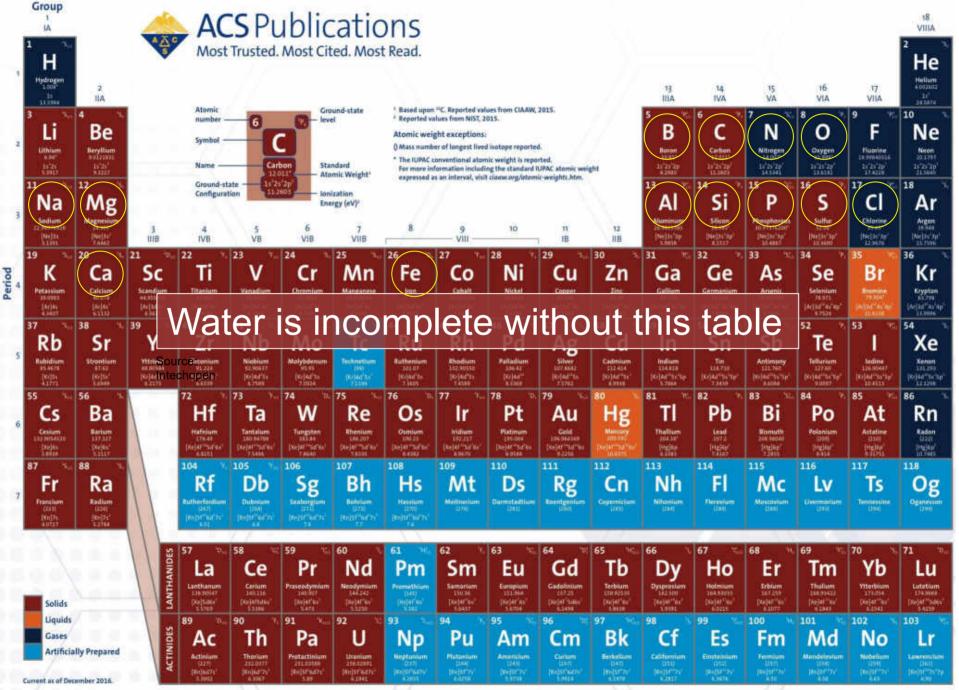
- 1. Patents: A method of preparing purified water from water containing pesticides, Indian patent 200767
- 2. Extraction of malatheon and chlorpiryhphos from drinking water by nanoparticles , US 7,968,493 A method for decontaminating water containing pesticides, **EP 17,15,947** Product is marketed now by a Eureka Forbes Ltd. Several new technologies are now available

#### Future of water purification: An enigma with some pointers



## Category-wise distribution of contaminants regulated by USEPA and future contaminants

Noble metal nanoparticles for water purification: A critical review, T. Pradeep and Anshup, Invited critical review, Thin Solid Films, 517 (2009) 6441-6478 (DOI: 10.1016/j.tsf.2009.03.195).



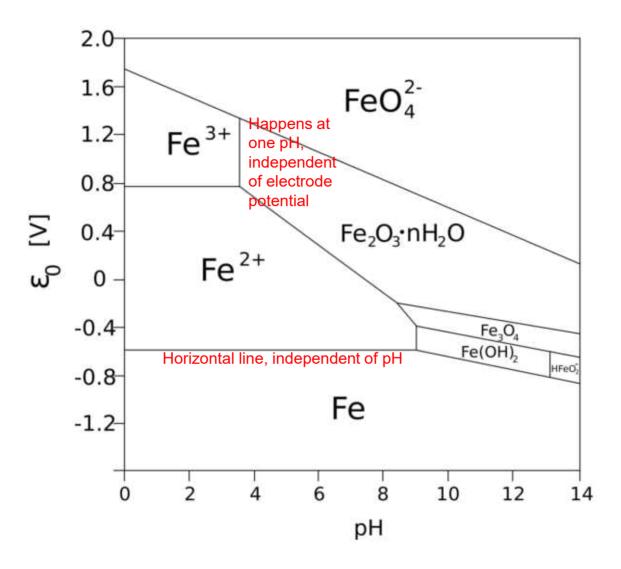
AB(s) = A+(aq) + B-(aq)

 $\mathsf{Ksp} = [\mathsf{A}+][\mathsf{B}-]$ 

#### Solubility-Product Constants, K<sub>sp</sub>, at 25°C

Fluorides		Chromates (co	Chromates (cont.)		Hydroxides (cont.)	
BaF <sub>2</sub>	$2.4 \times 10^{-6}$	Ag <sub>2</sub> CrO <sub>4</sub>	$1.9 \times 10^{-12}$	Ni(OH) <sub>2</sub>	1.6 × 10 <sup>-16</sup>	
MgF <sub>2</sub>	8 × 10-6	PbCrO <sub>4</sub>	$2 \times 10^{-16}$	Zn(OH) <sub>2</sub>	$4.5 \times 10^{-17}$	
PbF <sub>2</sub>	4 × 10 <sup>-8</sup>	Carbonates		Cu(OH) <sub>2</sub>	$1.6 \times 10^{-19}$	
SrF <sub>2</sub>	$7.9 \times 10^{-10}$	NiCO <sub>3</sub>	$1.4 \times 10^{-3}$	Hg(OH) <sub>2</sub>	3 × 10-26	
CaF <sub>2</sub>	$3.9 \times 10^{-11}$			Sn(OH) <sub>2</sub>	3 × 10-27	
Chlorides		CaCO <sub>3</sub> BaCO <sub>3</sub>	4.7 × 10 <sup>-9</sup> 1.6 × 10 <sup>-9</sup>	Cr(OH) <sub>3</sub>	$6.7 \times 10^{-31}$	
PbCl <sub>2</sub>	$1.6 \times 10^{-6}$	SrCO <sub>3</sub>	7 × 10-10	AI(OH) <sub>a</sub>	5 × 10-33	
AgCl	$1.7 \times 10^{-10}$	CuCO <sub>3</sub>	2.5 × 10 <sup>-10</sup>	Fe(OH) <sub>3</sub>	6 × 10-38	
Hg <sub>2</sub> Cl <sub>2</sub> e	$1.1 \times 10^{-16}$	ZnCO <sub>3</sub>	2 × 10 <sup>-10</sup>	Co(OH) <sub>3</sub>	$2.5 \times 10^{-43}$	
Bromides		MnCO <sub>3</sub>	8.8 × 10 <sup>-11</sup>	Sulfides		
PbBr <sub>2</sub>	$4.6 \times 10^{-6}$	FeCO <sub>3</sub>	2.1 × 10-11	MnS	7 × 10 <sup>-16</sup>	
AgBr	5.0 × 10 <sup>-13</sup>	Ag <sub>2</sub> CO <sub>3</sub>	8.2 × 10 <sup>-12</sup>	FeS	4 × 10 <sup>-19</sup>	
Hg <sub>2</sub> Br <sub>2</sub> *	1.3 × 10-22	CqCO3	5.2 × 10 <sup>-12</sup>	NiS	3 × 10-21	
lodides		PbCO <sub>3</sub>	1.5 × 10 <sup>-15</sup>	CoS	5 × 10 <sup>-22</sup>	
Pbl.	$8.3 \times 10^{-9}$	MgCO <sub>3</sub>	1 × 10 <sup>-15</sup>	ZnS	$2.5 \times 10^{-22}$	
Agl	8.5 × 10 <sup>-17</sup>	Hg <sub>2</sub> CO <sub>3</sub>	9.0 × 10 <sup>-15</sup>	SnS	1 × 10-24	
Hg <sub>2</sub> l <sub>2</sub> *	4.5 × 10 <sup>-29</sup>	OTO ACTO POSITIVO	0.00 % 10	CdS	$1.0 \times 10^{-28}$	
	70 10	Hydroxides		PbS	7 × 10 <sup>-29</sup>	
Sulfates	2.4. > 10-5	Ba(OH) <sub>2</sub>	$5.0 \times 10^{-3}$	CuS	8 × 10 <sup>-37</sup>	
CaSO <sub>4</sub>	2.4 × 10-5	Sr(OH) <sub>2</sub>	$3.2 \times 10^{-4}$	Ag <sub>2</sub> S	5.5 × 10-51	
Ag <sub>2</sub> SO <sub>4</sub>	1.2 × 10-5	Ca(OH) <sub>2</sub>	$1.3 \times 10^{-6}$	HgS	$1.6 \times 10^{-54}$	
SrSO <sub>4</sub>	7.6 × 10-7	AgOH	$2.0 \times 10^{-8}$	Bi <sub>2</sub> S <sub>3</sub>	$1.6 \times 10^{-72}$	
PbSO <sub>4</sub>	1.3 × 10-8	Mg(OH) <sub>2</sub>	$8.9 \times 10^{-12}$	Phosphates		
BaSO <sub>4</sub>	$1.5 \times 10^{-9}$	Mn(OH) <sub>2</sub>	$2 \times 10^{-13}$	Ag <sub>3</sub> PO <sub>4</sub>	$1.8 \times 10^{-18}$	
Chromates		Cd(OH) <sub>2</sub>	2.0 × 10-14	$Sr_3(PO_4)_2$	$1 \times 10^{-31}$	
SrCrO <sub>4</sub>	$3.6 \times 10^{-6}$	Pb(OH) <sub>2</sub>	$4.2 \times 10^{-15}$	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1.3 \times 10^{-32}$	
Hg <sub>2</sub> CrO <sub>4</sub> *	2 × 10-9	Fe(OH) <sub>2</sub>	$1.8 \times 10^{-15}$	Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6 × 10-39	
BaCrO <sub>4</sub>	8.5 × 10-11	Co(OH) <sub>2</sub>	$2.5 \times 10^{-16}$	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1 × 10-54	

<sup>\*</sup>As  $\mathrm{Hg_2^2+ion}$ .  $K_\mathrm{sp}=[\mathrm{Hg_2^2+}][\mathrm{X^-}]^2$ 



Pourbaix diagram of iron.

#### Toxic elements

Most popular heavy metals: lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As).

Commonly: arsenic, cadmium, chromium, lead, and mercury

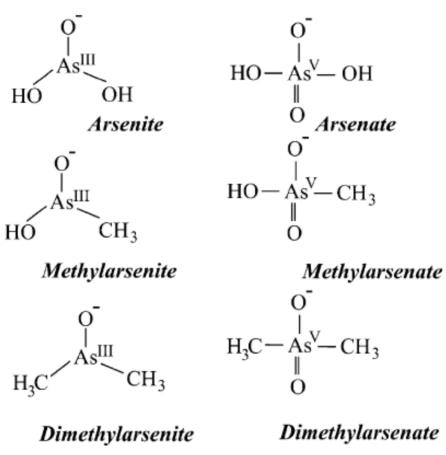
Why are they toxic?



Arsenopyrite FeAsS

Fe<sup>3+</sup>(AsS)<sup>3-</sup>or FeAsS

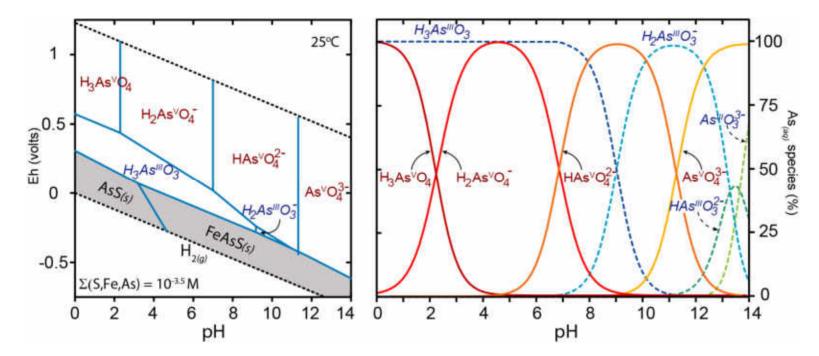
### Arsenic species of relevance



Scheme 1. Arsenic species found in water.

53<sup>rd</sup> element in abundance, 1/5 ppm in Earth's crust

Average concentration in soil 1-40 mg/kg



**Figure 1.** Eh-pH activity diagram of arsenic species at 25 °C, 1 bar, (S, Fe, As) =  $10^{-3}$  M (**left**). Dashed lines bound the stability field of water, arsenate (As<sup>V</sup>) species are shown in red, arsenite (As<sup>III</sup>) species are shown in blue italics, solid phases are shown with a darkened background. The distribution of pH-dependent dissolved arsenic species are shown (**right**) with arsenate as red solid lines and red text and arsenite in dashed blue lines with blue italic text. Dissolved arsenic species become protonated at low pH and the charge on the oxyanion decreases. Under environmental conditions (pH  $\approx$  5–9), arsenate generally exists as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>, while arsenite is the uncharged molecule H<sub>3</sub>AsO<sub>3</sub><sup>0</sup>. Under highly reducing conditions and in the presence of high sulfur activity, solid-phase arsenic sulfides (e.g., AsS) are stable.





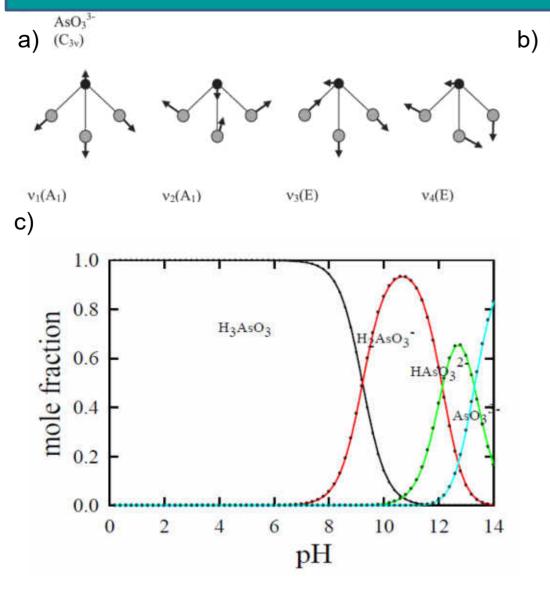
#### Arsenic in Drinking Water and Diabetes

Aryatara Shakya <sup>1</sup>, Matthew Dodson <sup>1</sup>, Janick F. Artiola <sup>2</sup>, Monica Ramirez-Andreotta <sup>2</sup>, Robert A. Root <sup>2</sup> Xinxin Ding <sup>1</sup>, Jon Chorover <sup>2</sup> and Raina M. Maier <sup>2</sup>.\*

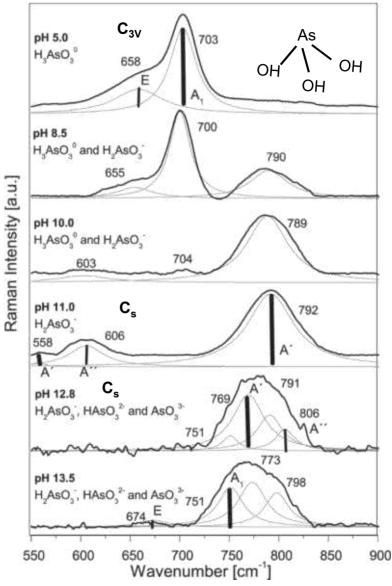
- Department Pharmacology & Toxicology, University of Arizona, Tucson, AZ 85721, USA; aryatarashakya@arizona.edu (A.S.); dodson@pharmacy.arizona.edu (M.D.);
- xding@pharmacyantzona.edu (X.D.)

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- chorover@arizona.edu (J.C.)

#### Distribution of arsenite species

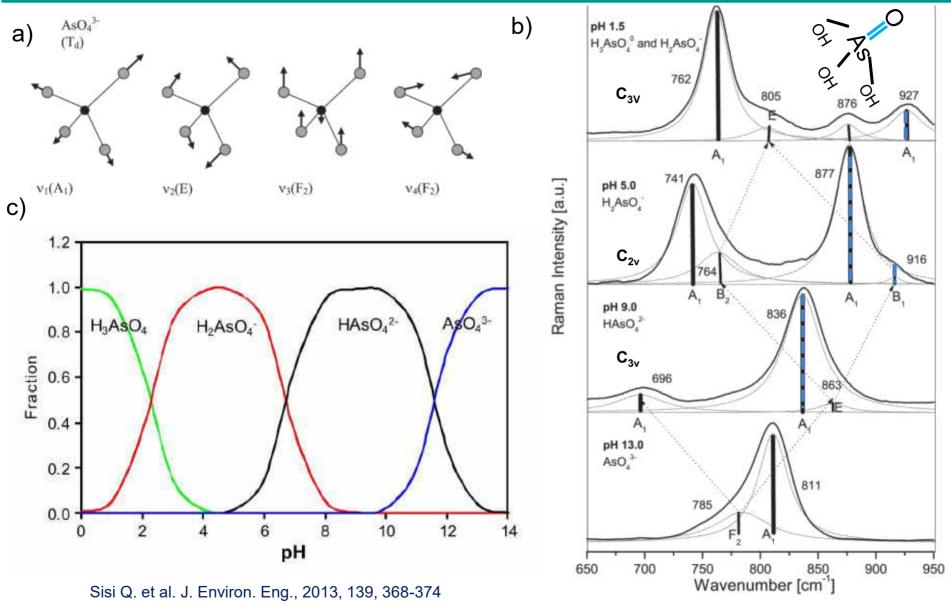


Inoue, K. Advances in Materials Physics and Chemistry, 2018, 8, 51-70.



Müller, K. et al. *Water research*, 2010, *44*, 5660 - 5667.

#### **Distribution of arsenate species**



Müller, K. et al. Water research, 2010, 44, 5660 -5667

### **Clean water for everyone**



ACS Sustainable Chemistry & Engineering Editorial, December 2016

#### Water positive materials

Biopolymer-reinforced synthetic granular nanocomposites for affordable point-of-use

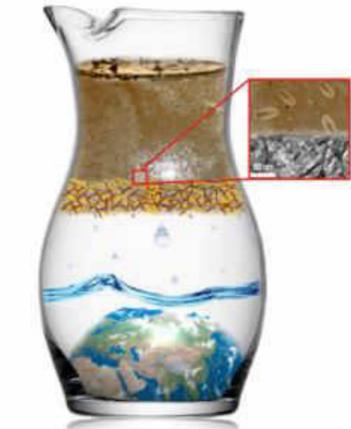
water purification

Mohan Udhaya Sankar<sup>1</sup>, Sahaja Aig Kamalesh Chaudhari, and Thalappil

Unit of Nanoscience and Thematic Unit of Ex-

Edited by Eric Hoek, University of California, I

Creation of affordable materials for const water is one of the most promising ways drinking water for all. Combining the composites to scavenge toxic species s other contaminants along with the abo affordable, all-inclusive drinking water ; without electricity. The critical probles synthesis of stable materials that can I uously in the presence of complex sp drinking water that deposit and cause surfaces. Here we show that such cons be synthesized in a simple and effective f out the use of electrical power. The masand-like properties, such as higher shear forms. These materials have been used water purifier to deliver dean drinking v ily. The ability to prepare nanostructur ambient temperature has wide releva water purification.



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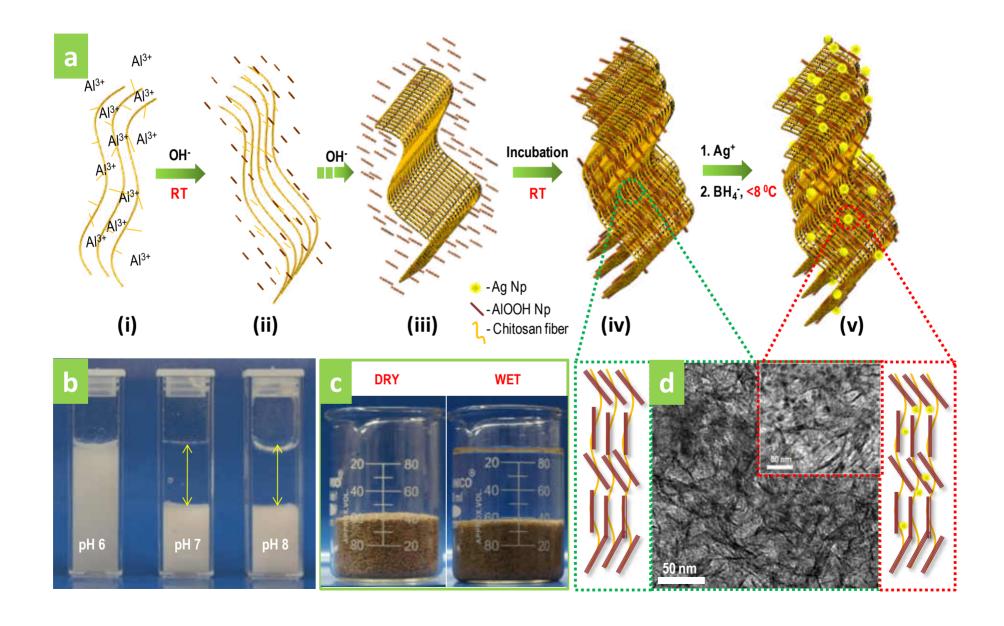
ew November 21, 2012)

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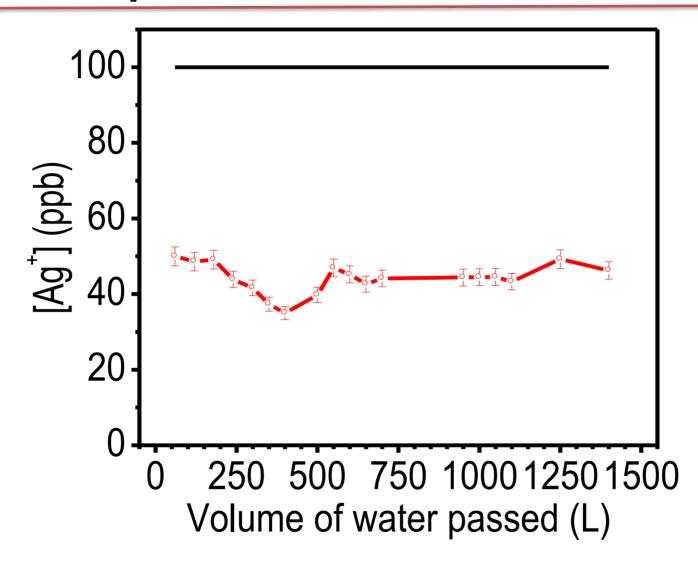
mily of nanocrystalline sposite materials prein aqueous route. The ibuted to abundant -Ohich help in the crysensure strong covalent matrix. X-ray photothe composition is rich rspectral imaging, the water was confirmed be silver nanoparticle al activity in drinking en developed that can e demonstrate an afn such composites defield trials in India, as tion of the waterborne

hybrid | green | appropriate technology | frugal science | developing works

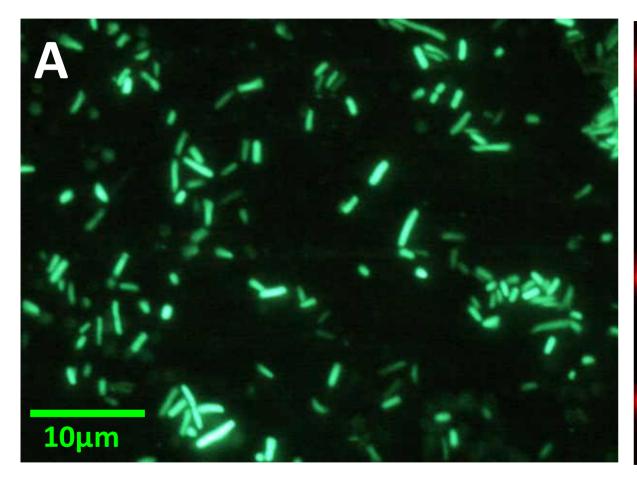
### How to make?

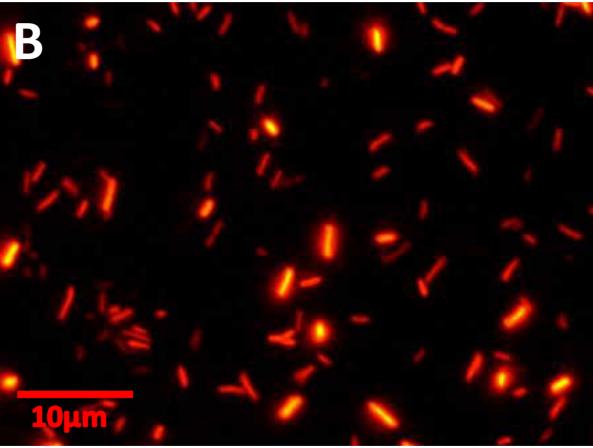


### What is special?

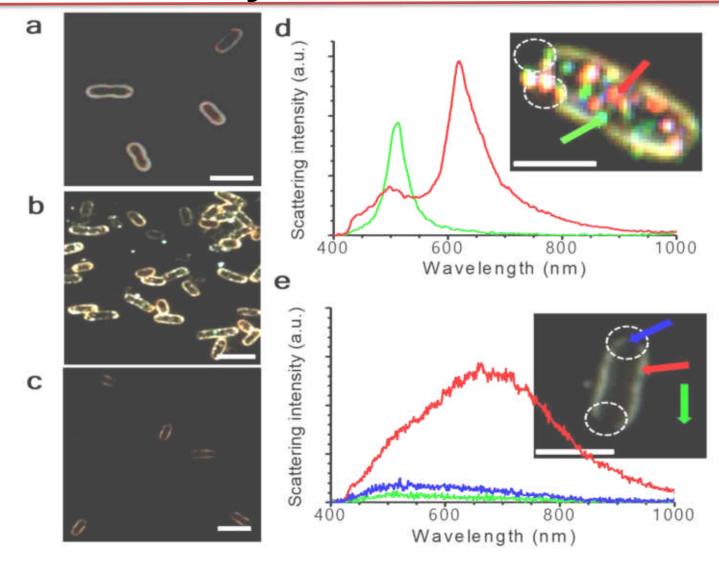


## Live/dead staining experiments

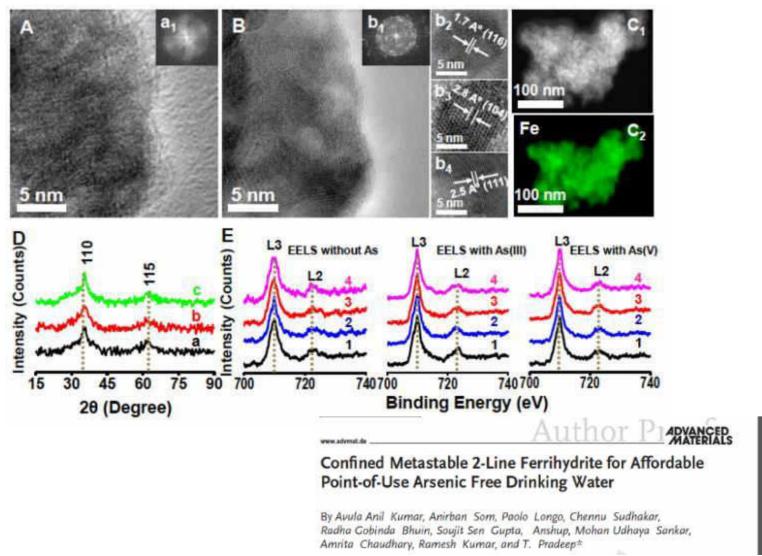




### No nanotoxicity



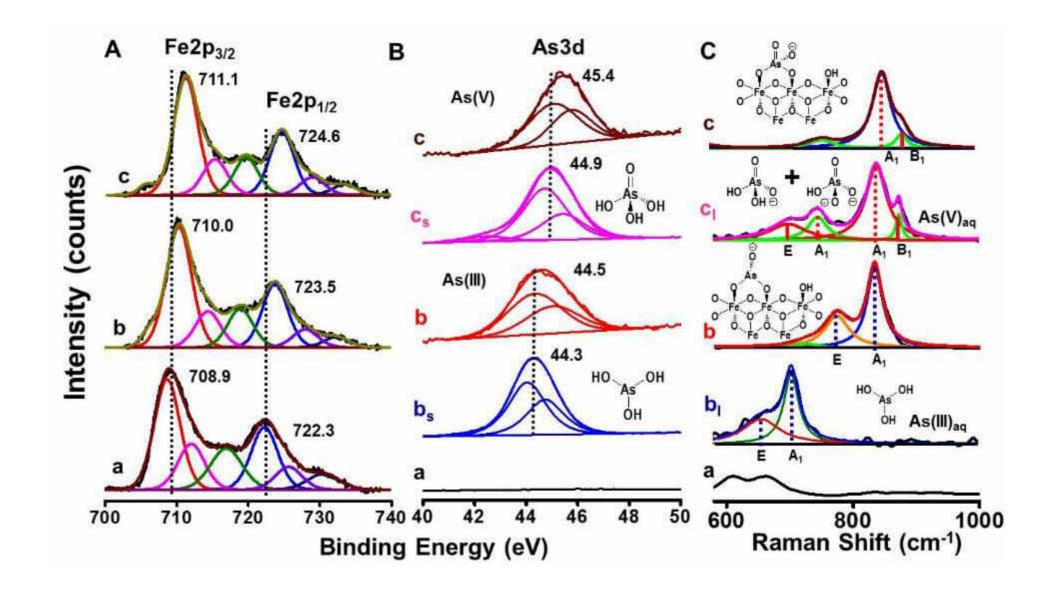
### **Variety of materials**



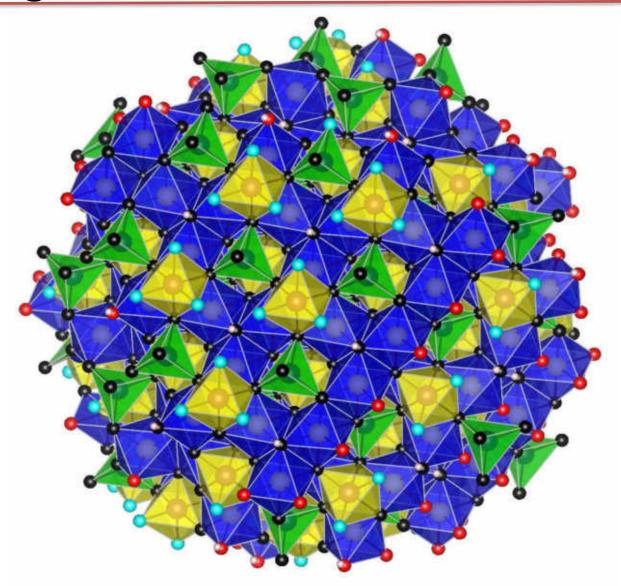
A. Anil Kumar, et. al. Adv. Mater., 29 (2016) 1604260.

mmunication

### **Mechanism**

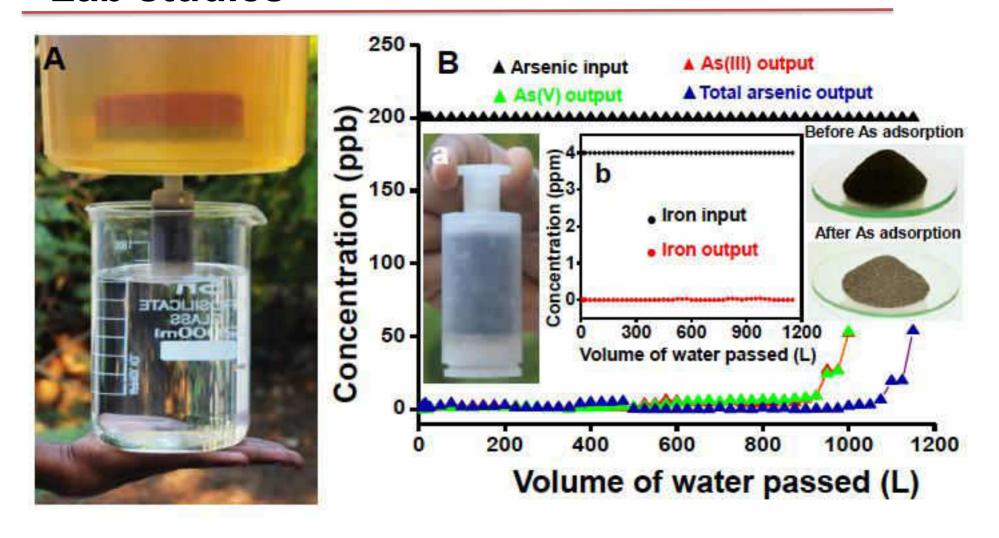


## **Modeling surfaces**



Chennu Sudhakar, et al. ACS Sustainable Chemistry & Engineering, 6 (2018) 9990-10000.

#### Lab studies

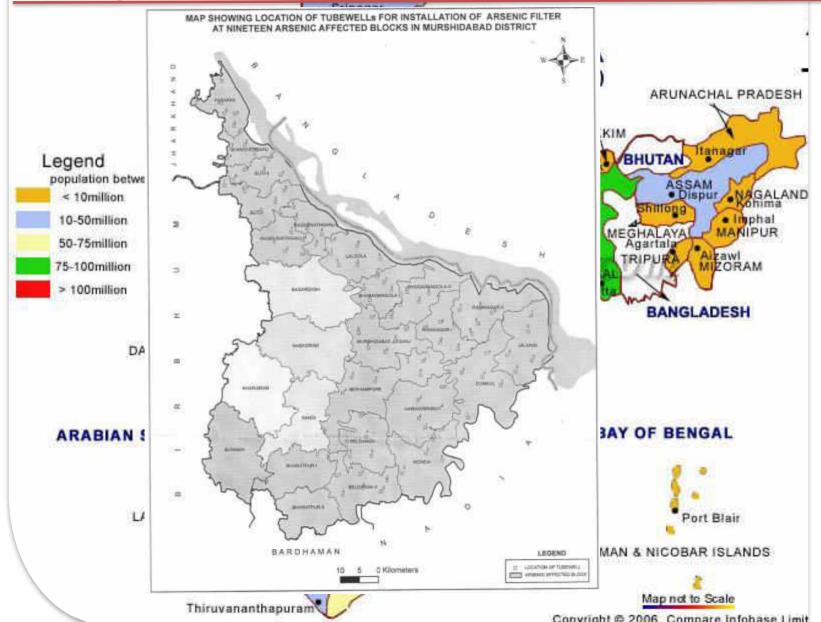


## Initial pilot studies

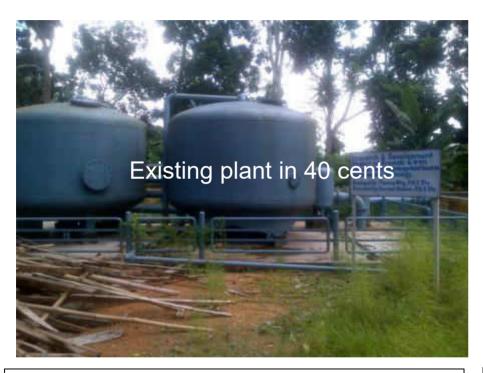


# Larger pilot studies

#### Population Map Of India-2001



### Changing the dynamics in the field



- Existing unit for iron and arsenic removal 20 m<sup>3</sup>/h
- Uses activated alumina and iron oxide (old generation of adsorbents)



- Existing unit for iron and arsenic removal 18 m³/h
- Uses iron oxyhydroxide (new generation of adsorbents)
- Input arsenic concentration: 168 ppb
- Output arsenic concentration: 2 ppb





#### Implementation - From 25 KLD to 1 MLD



Large water supply schemes

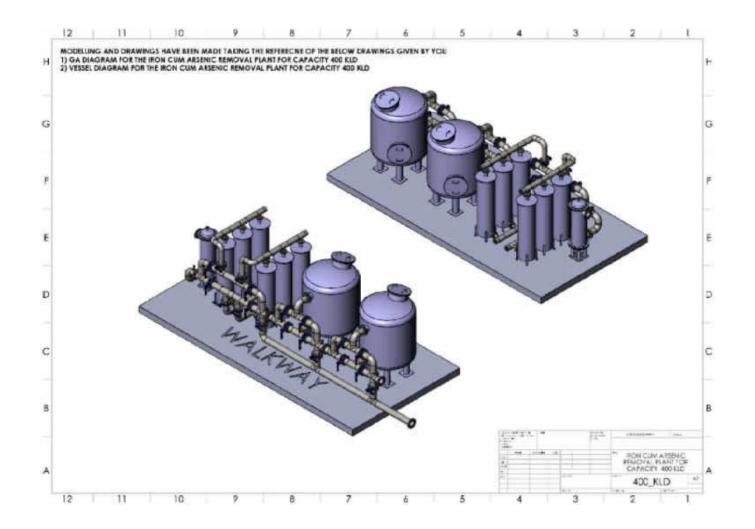
Capacity: above 1 MLD

5 schemes in use across India



Retrofitted Water Purification Plant Capacity: 0.1-1 MLD

Over 180 units in use across India



#### Cleanwater at 2.1 paise per litre!

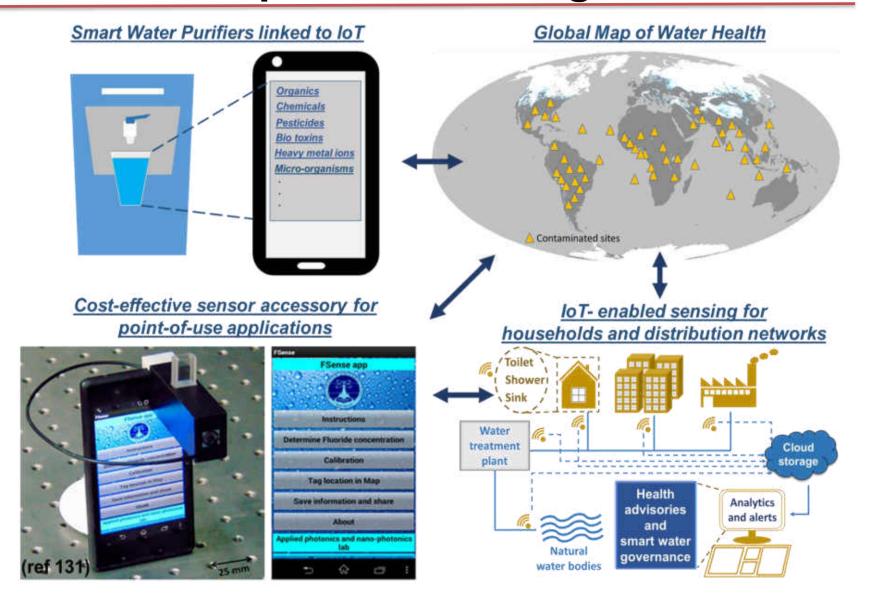
#### Calculation for the Tariff to be collected for treated water (Revision if Required)

	Design population	1,071	Plant capacity/70 LPCD
Sr.No	Item/Description	Cost / Quantity	Remarks
1	Cost of Replacement of Iron removal media	56400	After minimum two years if Iron concentration is more than 5 ppm. But iron concentration is more than 5 ppm at only two to three places. Therefore media may work for 3 years also.
2	Cost of Replacement of Arsenic removal media	978660	After minimum two years if Arsenic concentration is more than 100 ppb. But arsenic concentration is more than 100 ppb at only two to three places. Therefore media may work for 3 years also.
3	Cost of replacement of Activated Carbon	28560	
4	Total cost of Replacement of media	1063620	After minimum two years.
5	Total cost of Replacement of media for one year	531810	
6	Plant capacity	75000	ltr per day
7	Design population	1,071	Plant capacity/70 LPCD
8	Cost per litr of water	2.1 Paise per Itr	0.025 cents
9	Cost of replacement of media	1.36 <u>40.80</u>	Rs. per head per day =Media replacement cost per year/365/Design population per head per month for 70 LPCD water

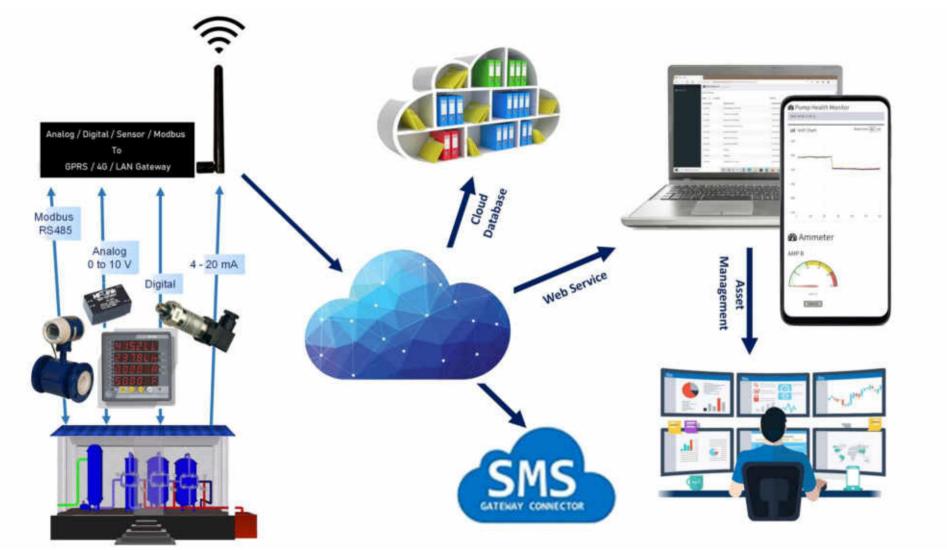
**Across the country** 



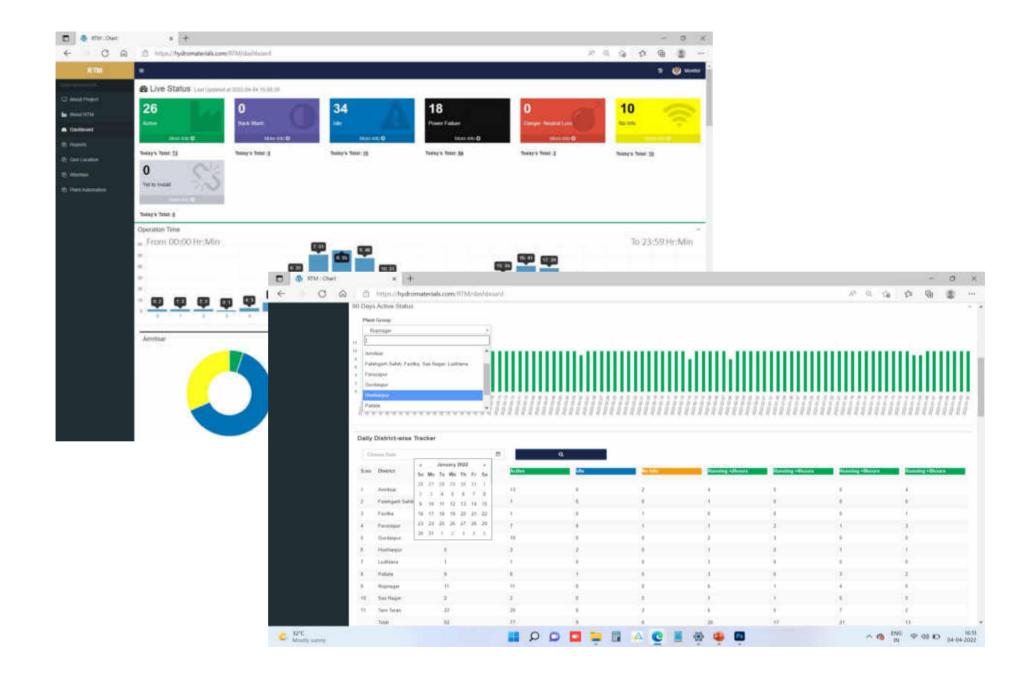
#### Smart water purifiers and big data

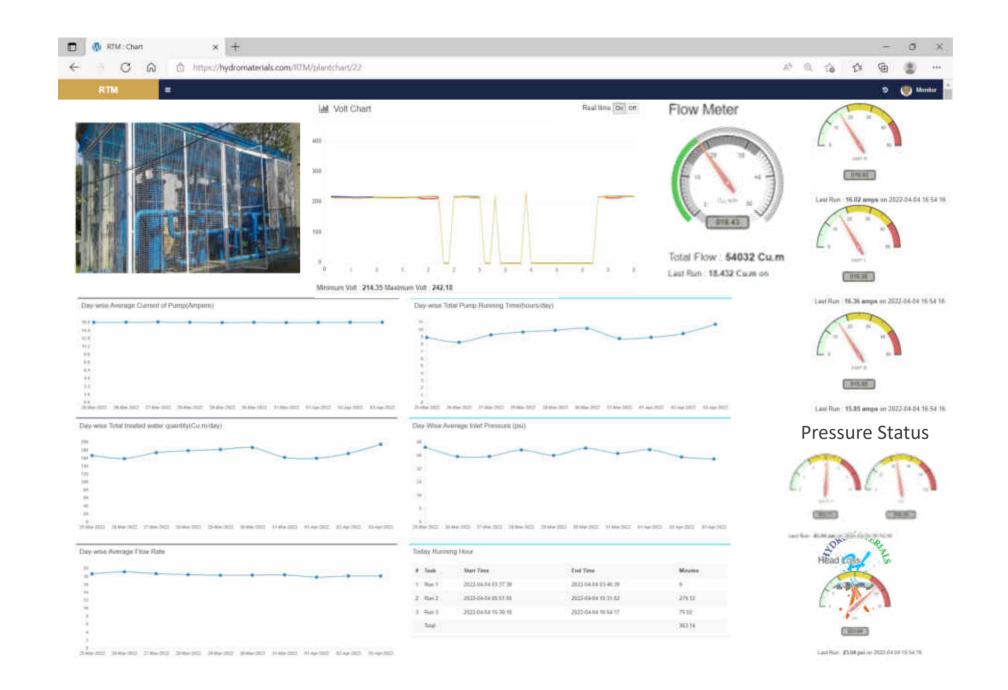


#### Components of IoT architecture implemented by DWSS, GoP









#### Clean water at 2.1 paise per litre!

	Calculation for the Tariff to be co	llected for treate	ed water (Revision if Required)
	Design population	1,071	Plant capacity/70 LPCD
Sr.No.	Item/Description	Cost / Quantity	Remarks
1	Cost of Replacement of Iron removal media	56400	After minimum two years if Iron concentration is more than 5 ppm. But iron concentration is more than 5 ppm at only two to three places. Therefore media may work for 3 years also.
2	Cost of Replacement of Arsenic removal media	978660	After minimum two years if Arsenic concentration more than 100 ppb. But arsenic concentration is more than 100 ppb at only two to three places. Therefore media may work for 3 years also.
3	Cost of replacement of Activated Carbon	28560	
4	Total cost of Replacement of media	1063620	After minimum two years.
5	Total cost of Replacement of media for one year	531810	
6	Plant capacity	75000	ltr per day
7	Design population	1,071	Plant capacity/70 LPCD
8	Cost per litr of water	2.1 Paise per ltr	0.025 cents
9	Cost of replacement of media	1.36	Rs. per head per day =Media replacement cost per year/365/Design population
	.,		

40.80

per head per month for 70 LPCD water

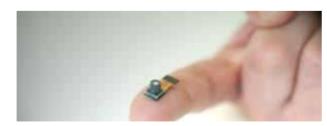
#### Sensors and new opportunities



Analog/Grating
Equipment
\$ 5~6 Billion (2017)
a few 100k units (2017)



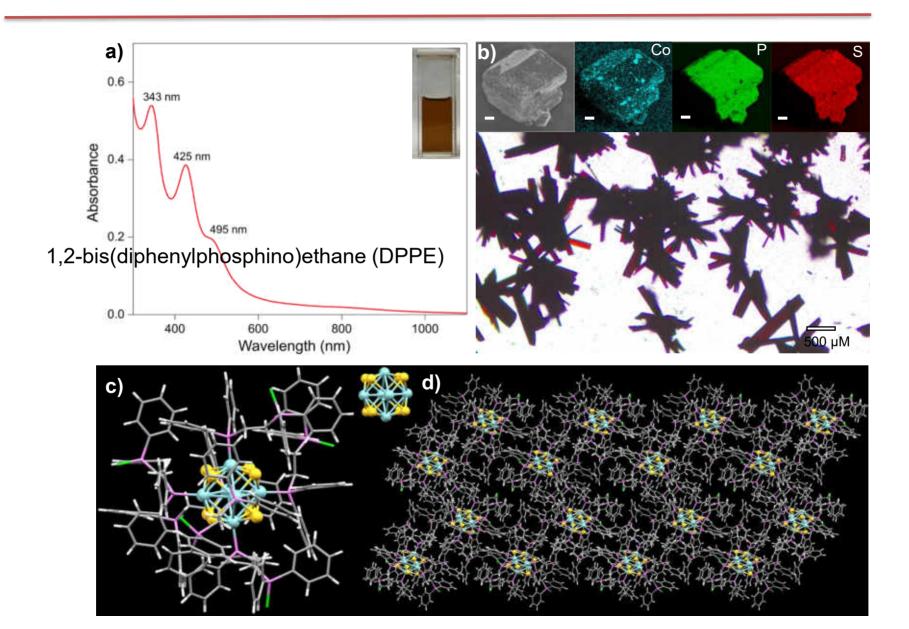
Ultra compact Low Cost Spectral Sensor Module ~ Billions units (? 2027)



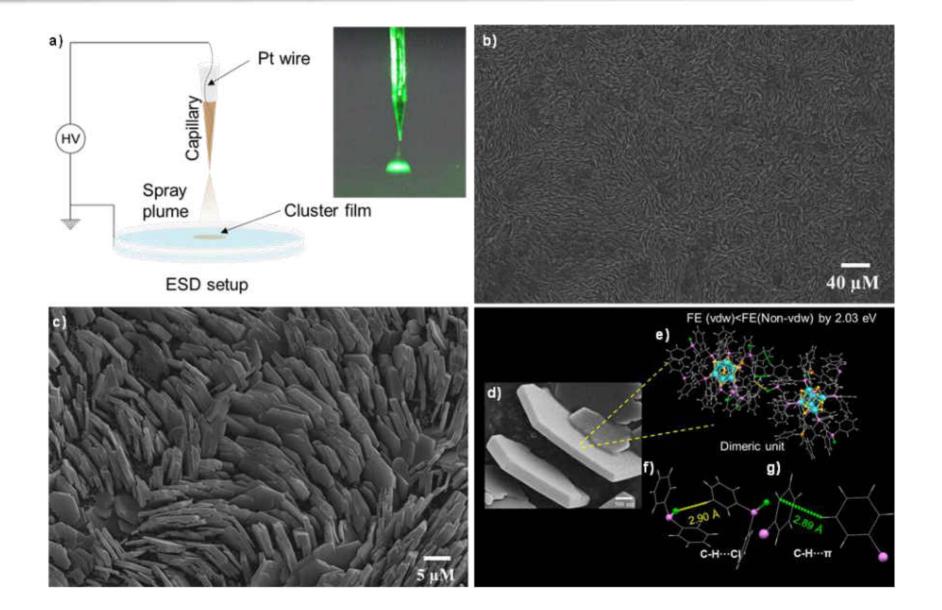


Water quality measurement – In the pipeline

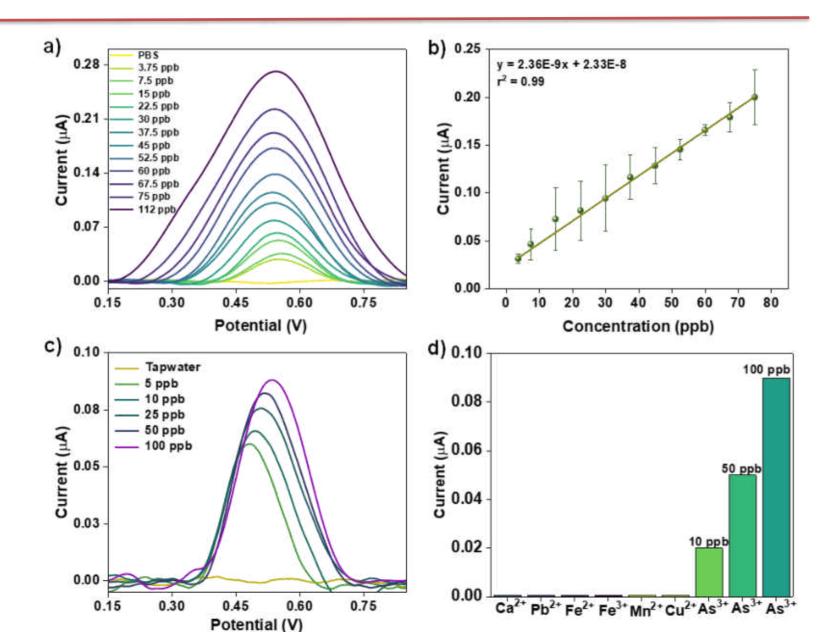
#### New electrodes - Aligned nanoplates of Co<sub>6</sub>S<sub>8</sub>



#### **Electrospray deposition**

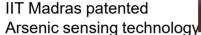


#### **Sensing**



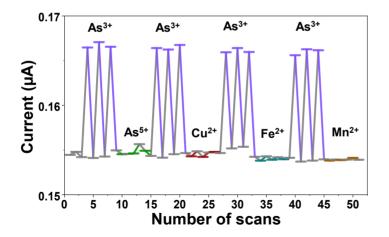
#### A drop-and-sense reagent free arsenic sensing test strips

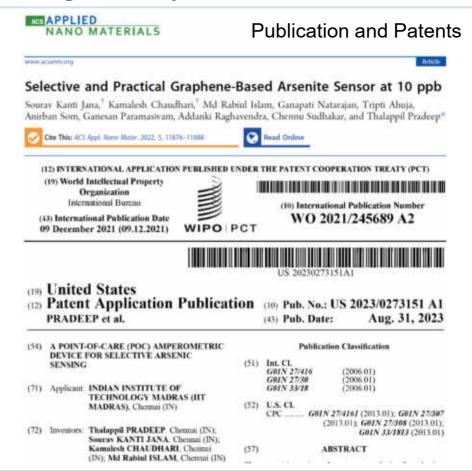






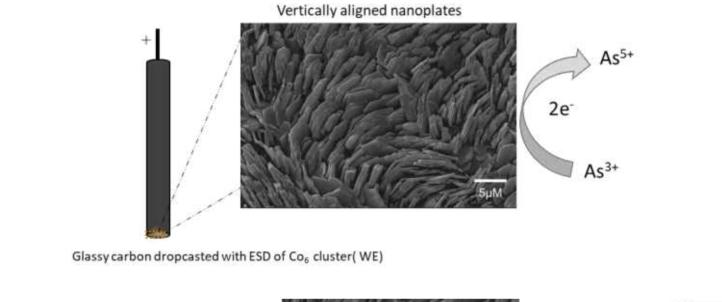
Reagent free, Reusable test strip with selective arsenic sensing Drop-and-sense technology with no pretreatment of samples

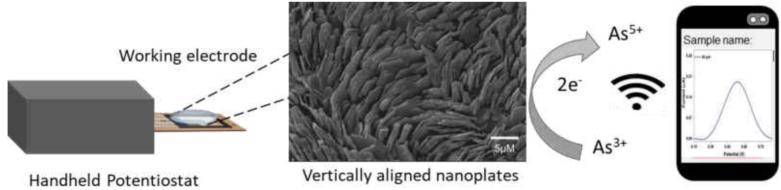






#### **Working electrode**





Anagha Jose et al. ACS Materials Lett., 5 (2023) 893–899.

#### Monitoring in the field

# EyeNetAqua Solutions Pvt. Ltd. An ICCW incubated company Eye of internet on quality, quantity and compliance for all

Installation model as per NJJM specifications

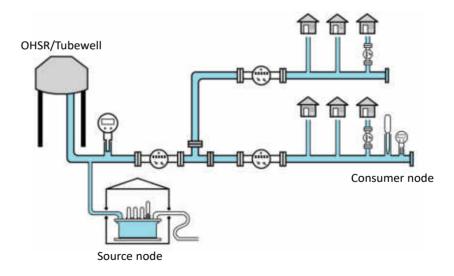
#### Tubewell/OHSR (Source node):

- 1. Flow meter (80-150mm) x 1
- 2. Pressure sensor x 1
- 3. pH sensor x 1
- 4. TDS sensor >
- 5. Residual Chlorine sensor x 1
- 6. In-house MVP of Free Residual Chlorine sensor x 1

#### Consumer tap (End tail node):

- 1. Flow meter (15-20mm) x 1
- 2. Pressure sensor x 1
- 3. Residual Chlorine sensor x 1
- 4. In-house MVP of Free Residual Chlorine sensor x 1



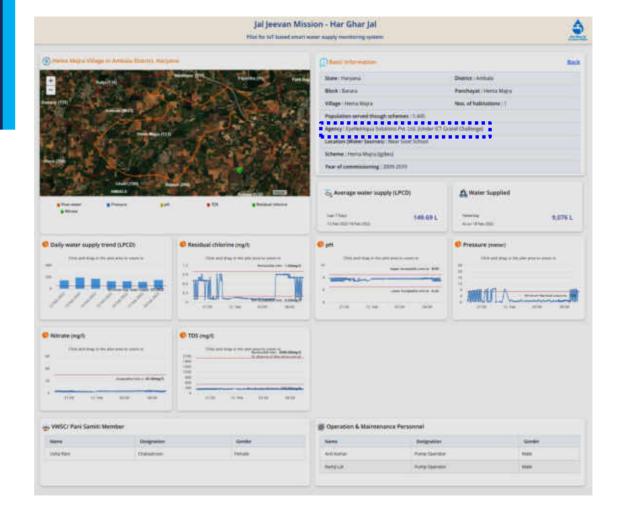


#### EyeNetAqua Solutions Pvt. Ltd.

An ICCW incubated company

Eye of internet on quality, quantity and compliance for all

# Real time water



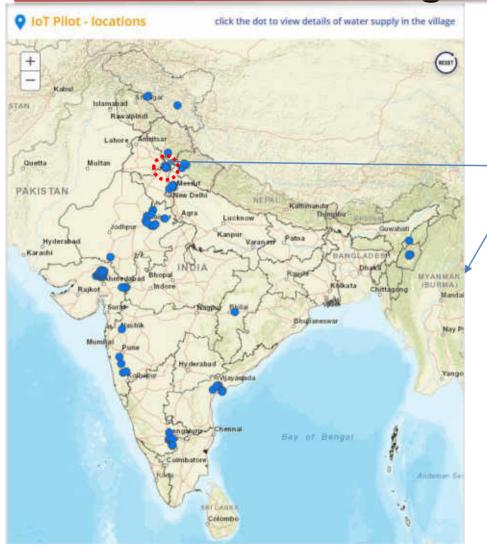


#### **Snapshot of water quality analysers**

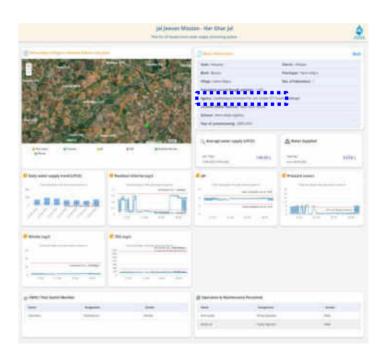




#### India's water is being monitored



IITM/IISc
Installations made by four companies

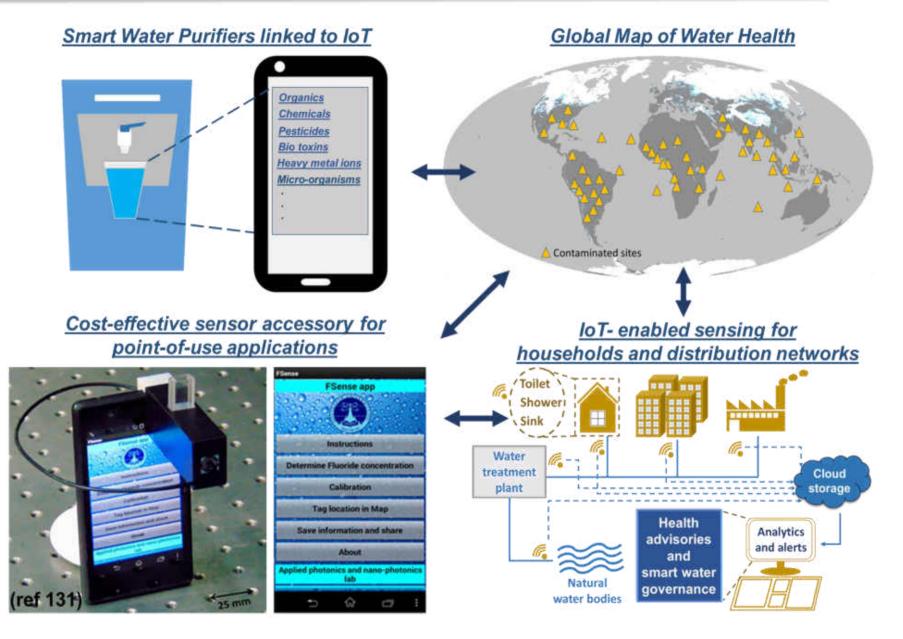


#### Mobile unit - A reagent free mobile water quality analyser

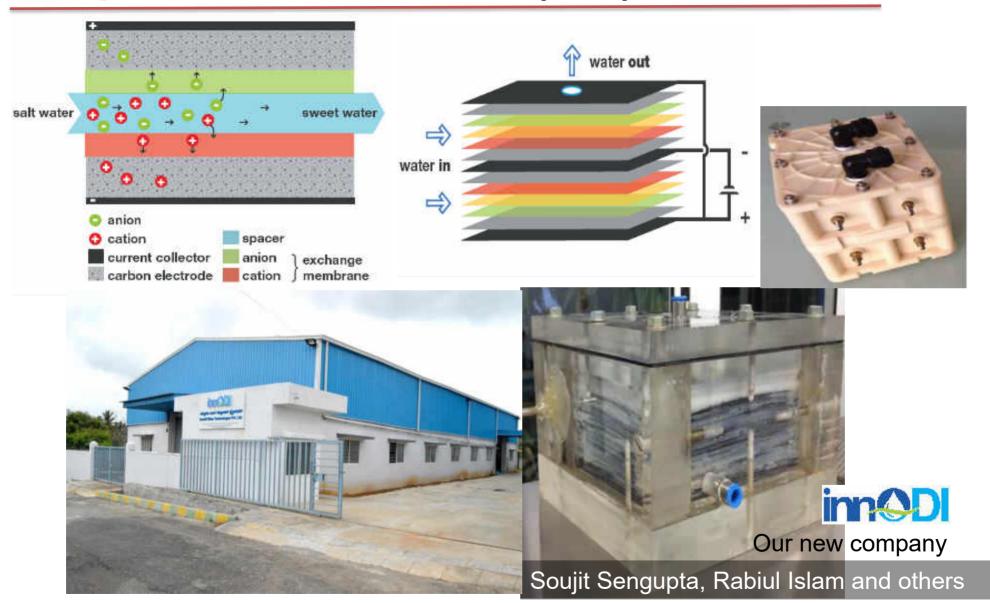




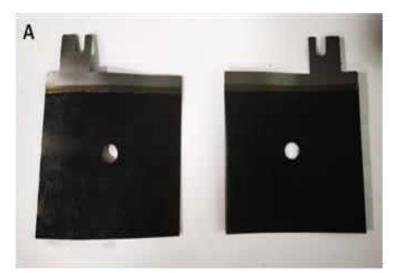
#### Smart water purifiers and big data

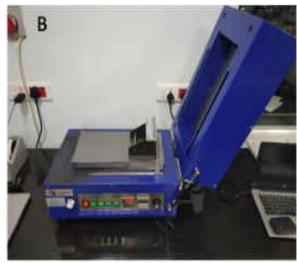


#### **Capacitive Desalination (CDI)**

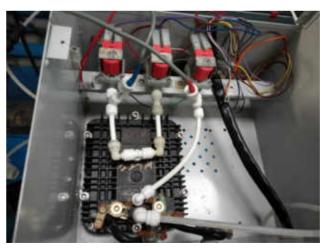


#### Various stages of electrode preparation

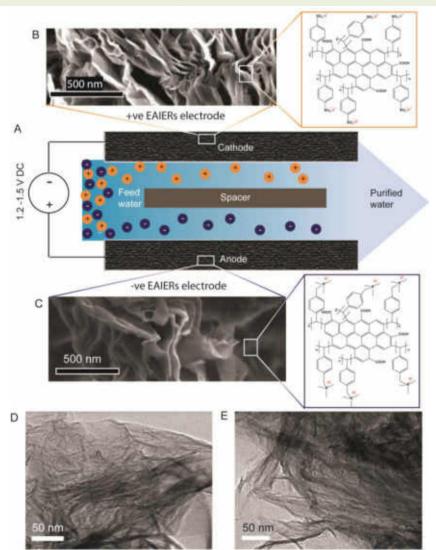








### A Covalently Integrated Reduced Graphene Oxide -Ion Exchange Resin Electrode for Efficient CDI



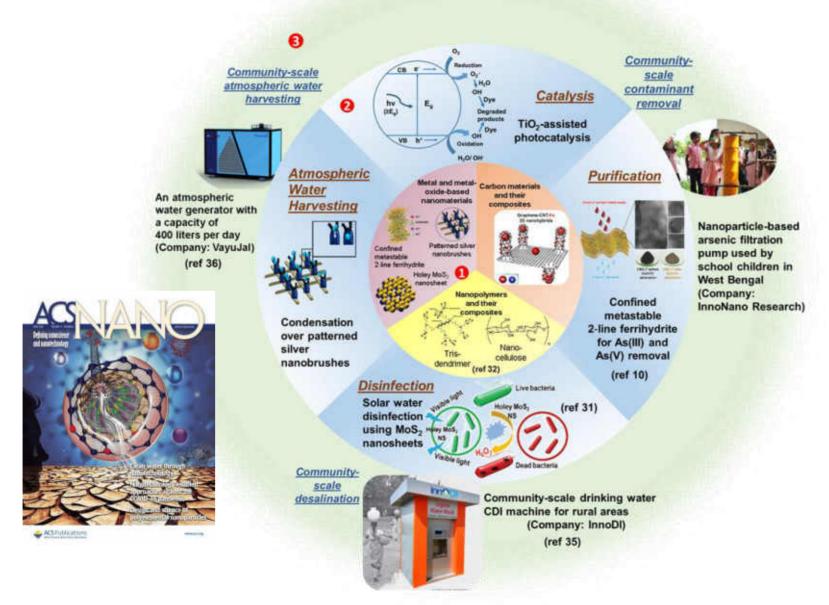
Rabiul et al., Adv. Mater. Interfaces 2021, 8, 2001998

#### DIGITAL WATER KIOSK

for community drinking using CDI Technology



#### **Evolution of materials to products**

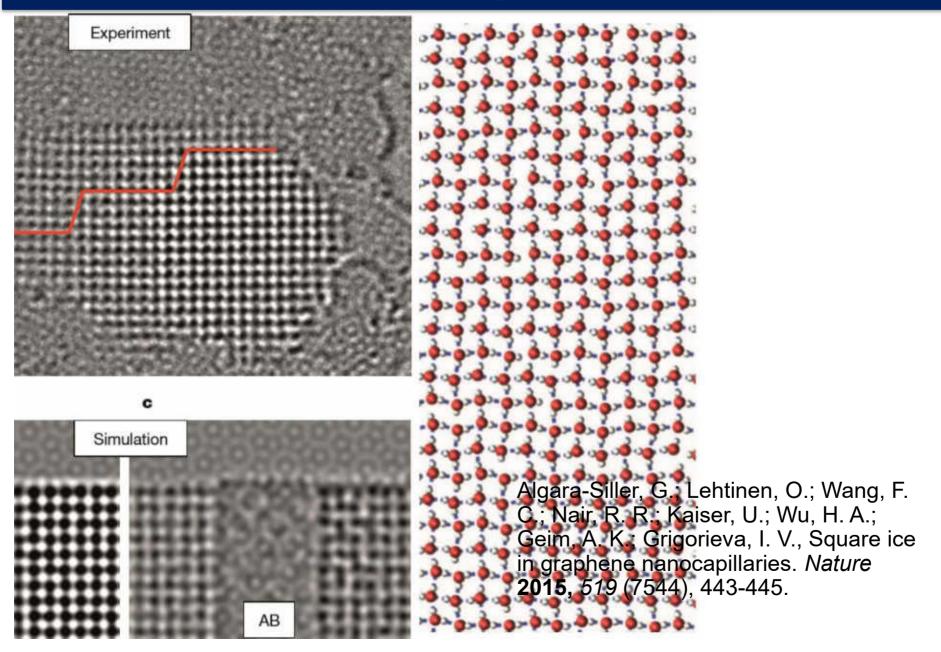


Ankit Nagar and T. Pradeep, ACS Nano 14 (2020) 6420-6435.





#### **Observing water**





## Indian Institute of Technology Madras





Bhaskar Ramamurthi/V. Kamakoti



