Fluoride Mitigation Options: Challenges and Opportunities

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Presentation Outline

1. Fluoride Contamination: from Global Perspectives

2. Fluoride distribution in water and its influence on water availability and access to safe water supply: The case of Ethiopia

3. The link between Total Dietary Fluoride Intake and observed Health Risks due to various forms of fluorosis

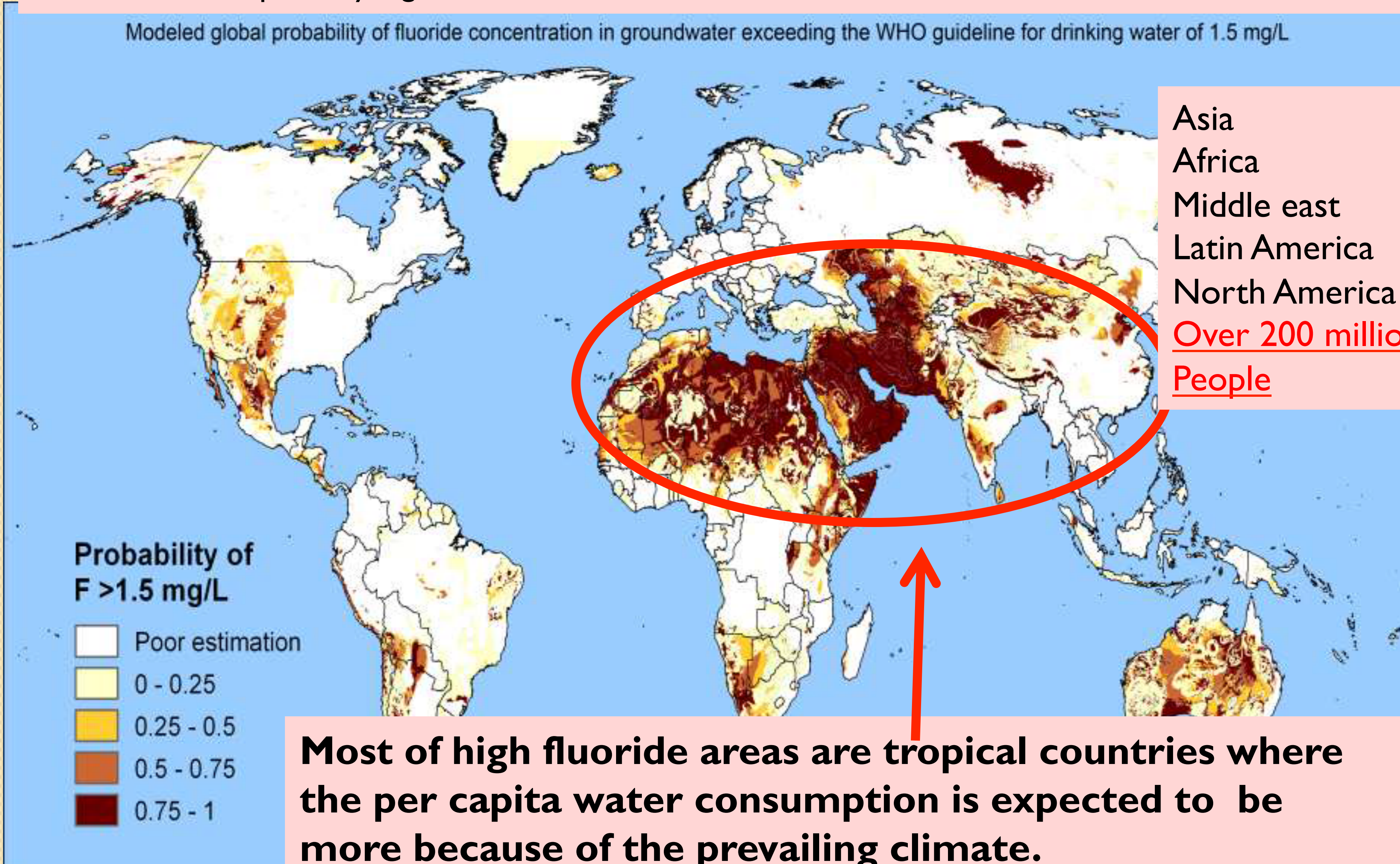
4. The urgent need to work on an integrated approach to mitigate fluorosis

5. New Fluoride Removal Technologies we are currently developing

6. Concluding remarks concerning the challenges and opportunities

Fluoride Contamination: Global Perspectives

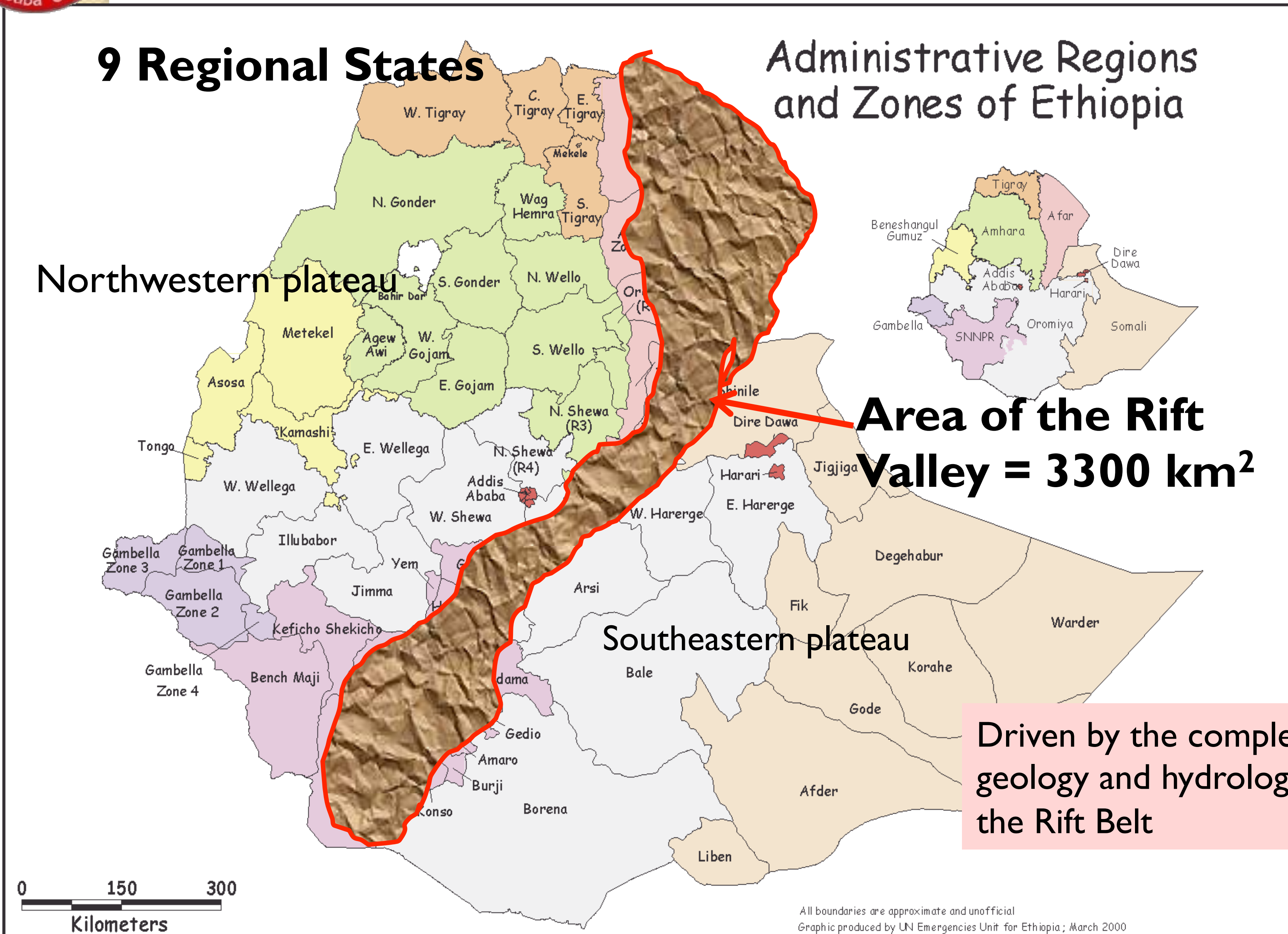
Fluoride exists in trace amounts in almost all groundwater throughout the world, but in some countries at exceptionally high level



Asia
Africa
Middle east
Latin America
North America
Over 200 million People

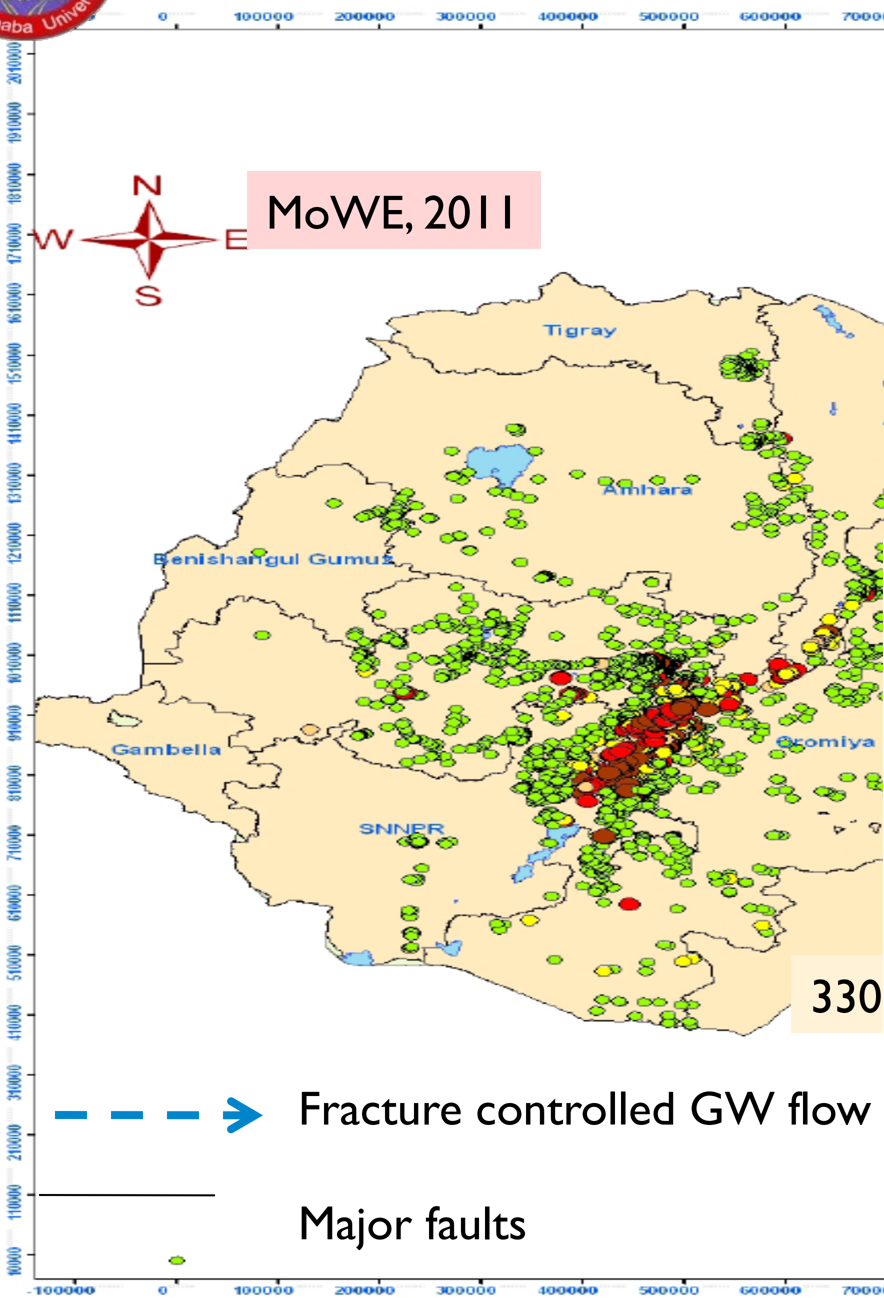
Most of high fluoride areas are tropical countries where the per capita water consumption is expected to be more because of the prevailing climate.

The High Fluoride Belt in Ethiopia

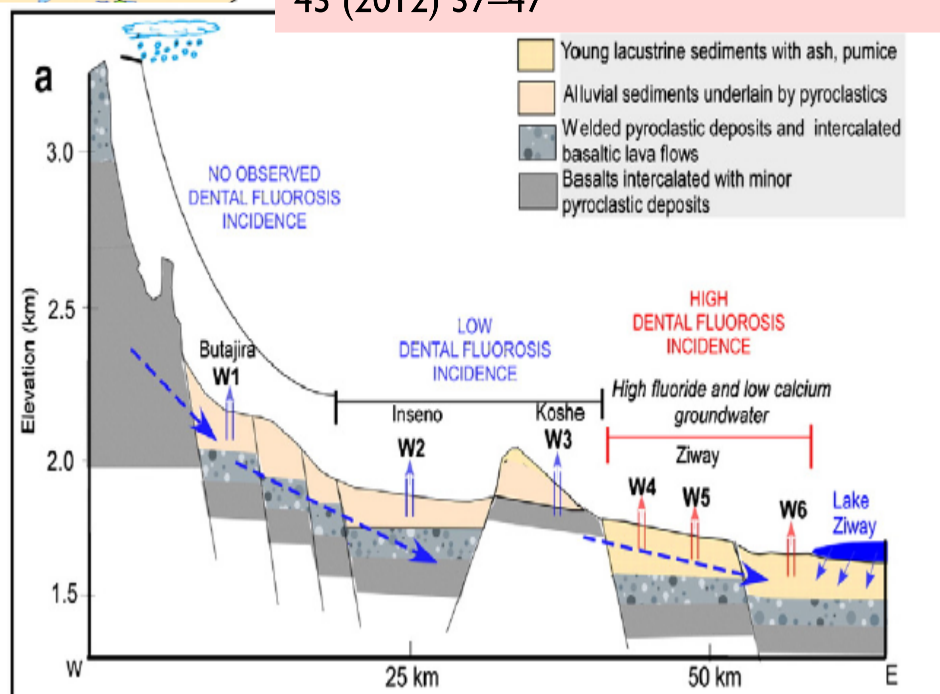


Driven by the complex geology and hydrology of the Rift Belt

Fluoride Distribution in Ethiopia



MoWE, 2011



T. Rango et al. / Environment International 43 (2012) 37–47

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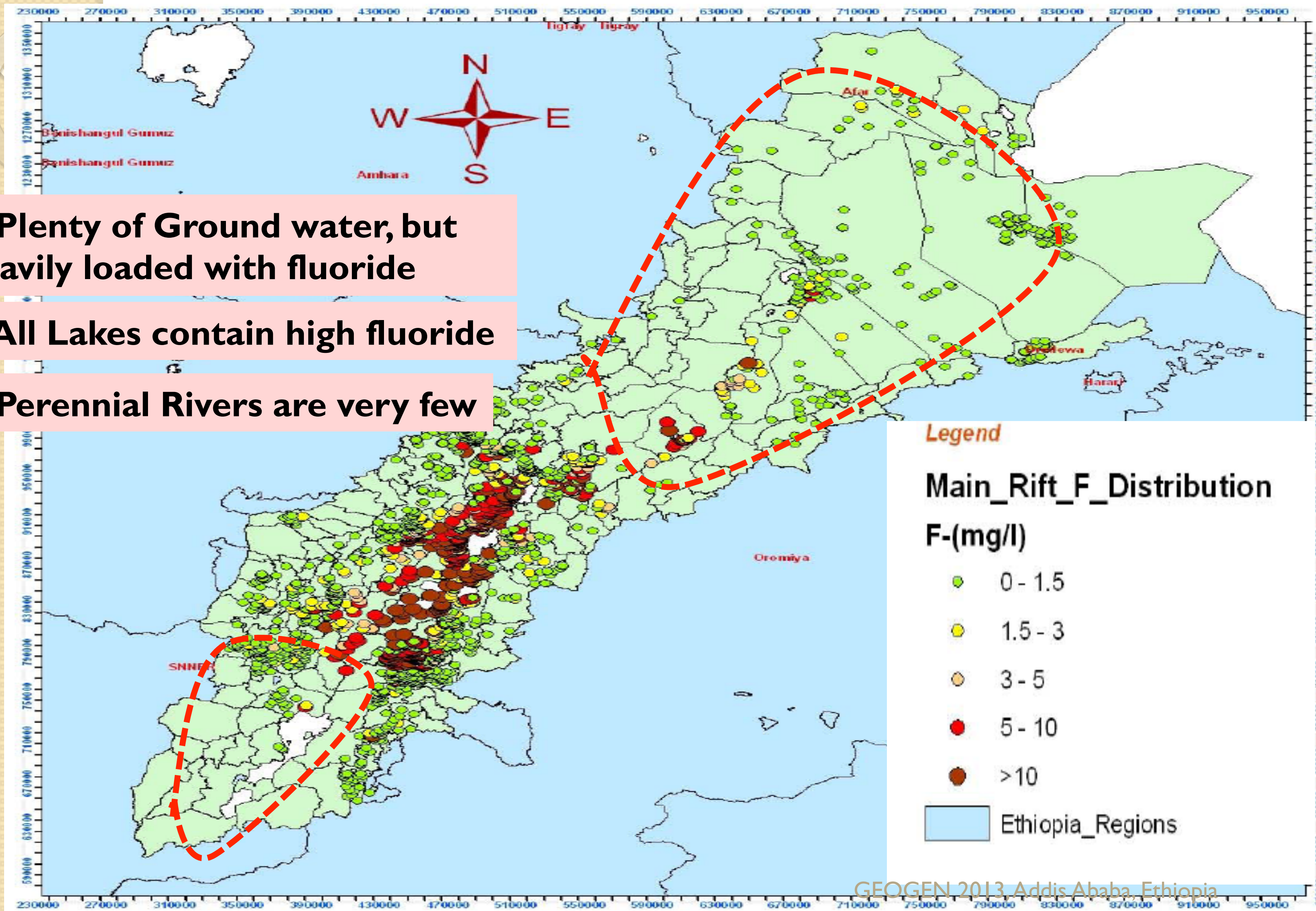
Fracture controlled GW flow

Major faults

Fluoride Distribution in Ethiopia (Cont'd)

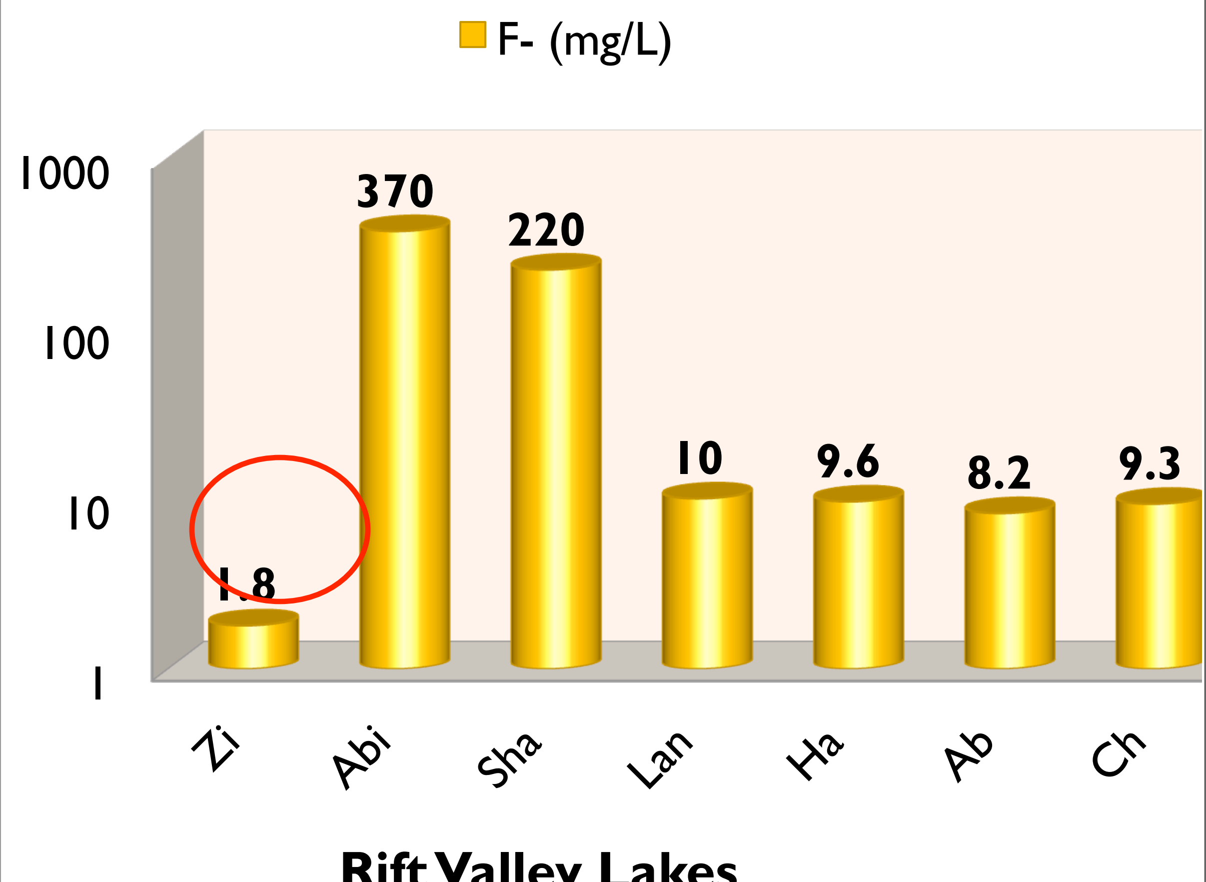


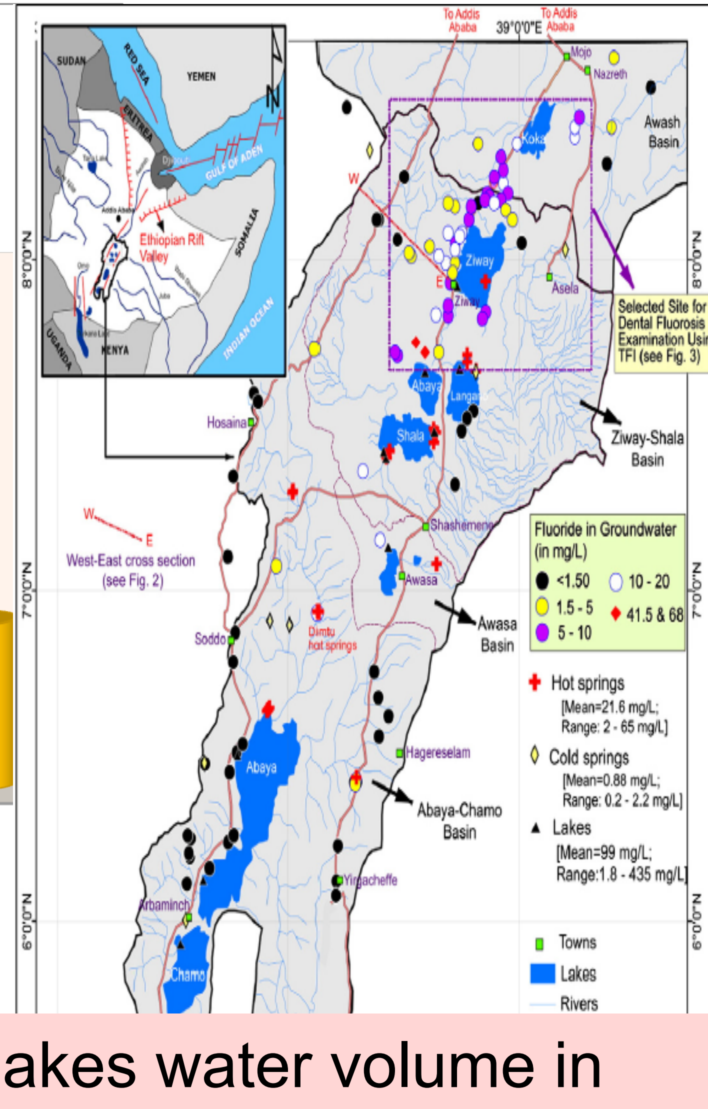
1. **Plenty of Ground water, but heavily loaded with fluoride**
2. **All Lakes contain high fluoride**
3. **Perennial Rivers are very few**

Fluoride Distribution in Ethiopia (Cont'd)

Fluoride Content of the Ethiopian Rift Valley Lakes

MoWE, 2013



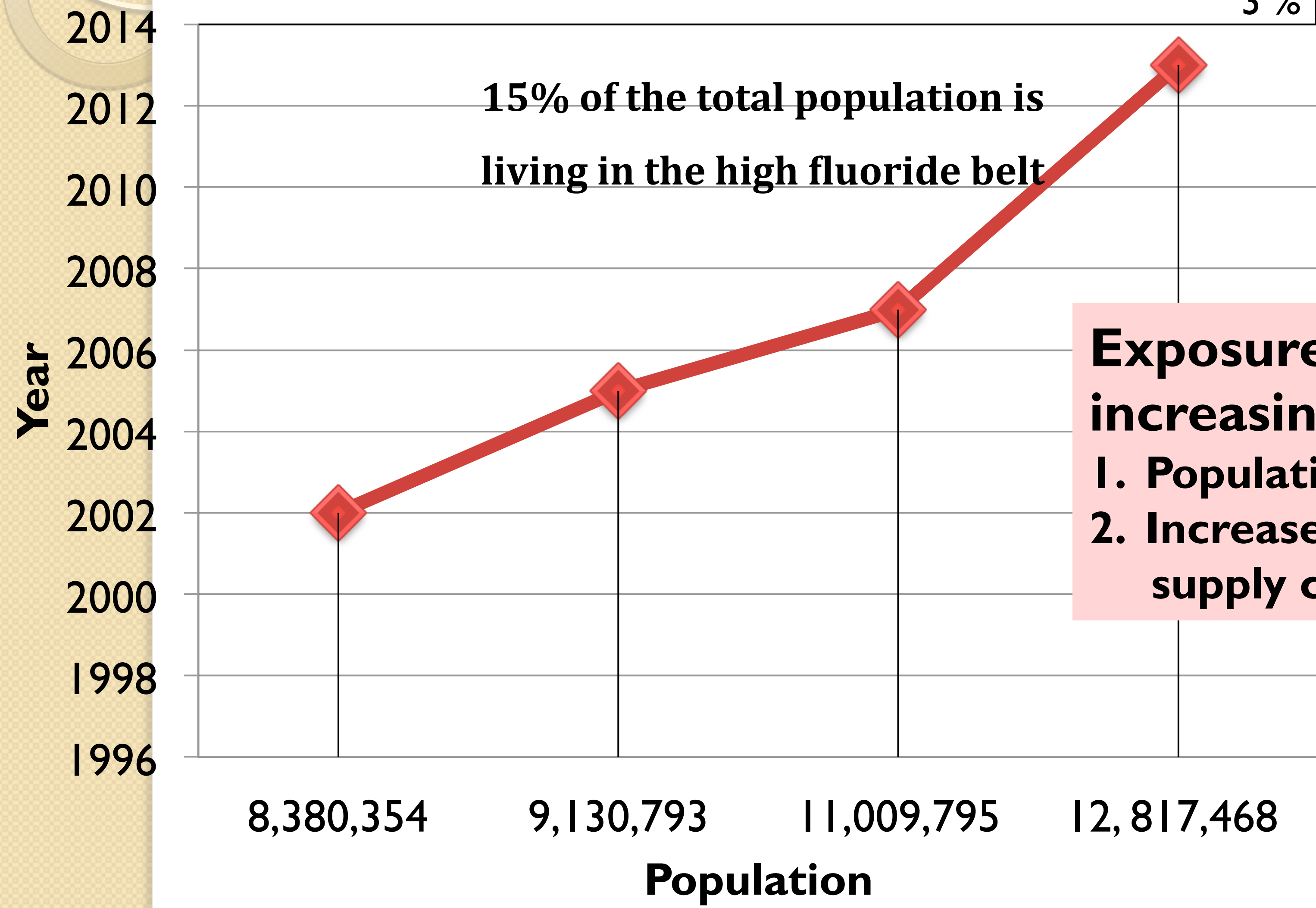


RV Lakes constitute about 60 % of lakes water volume in Ethiopia

Population Exposure to Fluoride

Total population of Ethiopia is about 85 Million

Growth rate of over 3 % per annum



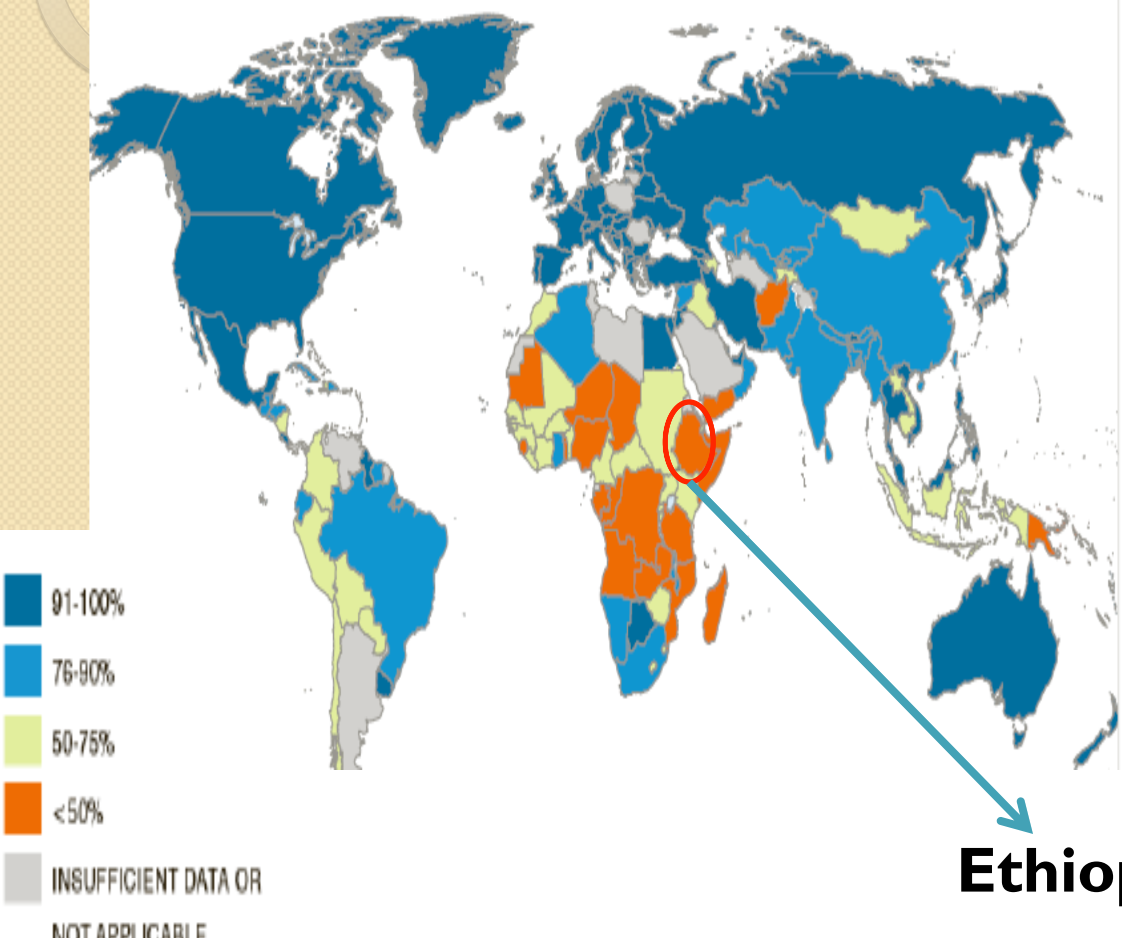
Exposure is increasing due to

1. **Population explosion**
2. **Increase in water supply coverage**

Water Supply Coverage: Ethiopia

768 million people use unimproved source

Rural Coverage



Urban Coverage

Ethiopia

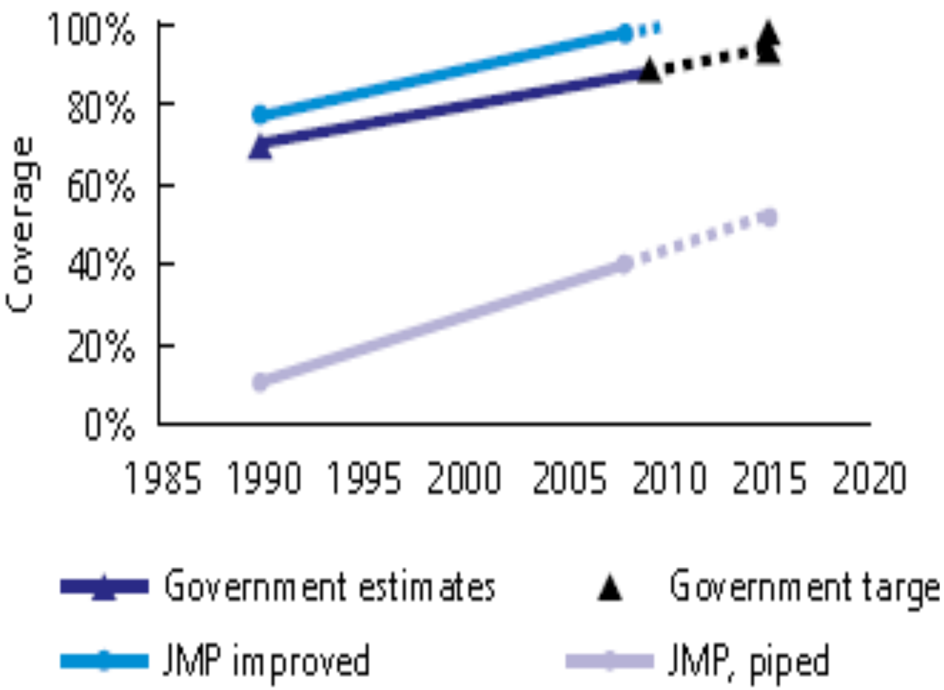
An "improved drinking-water source" is one that by the nature of its construction adequately protects the source from outside contamination, in particular from faecal matter.

Proportion of the population using improved drinking water (JMP 2010 report)

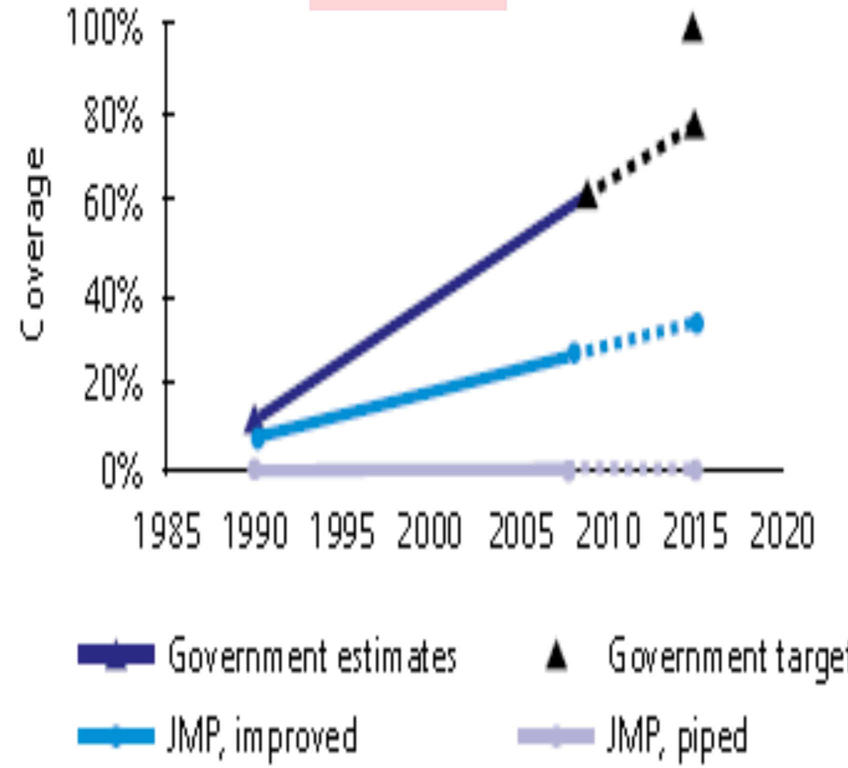
Water Supply Coverage: Ethiopia (Cont'd)

Urban-Rural Disparity

Urban



Rural

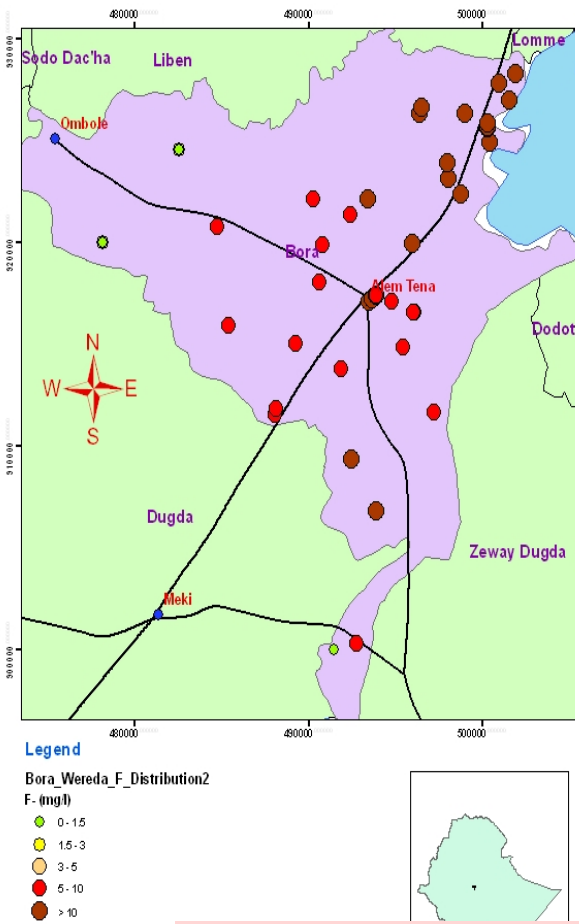


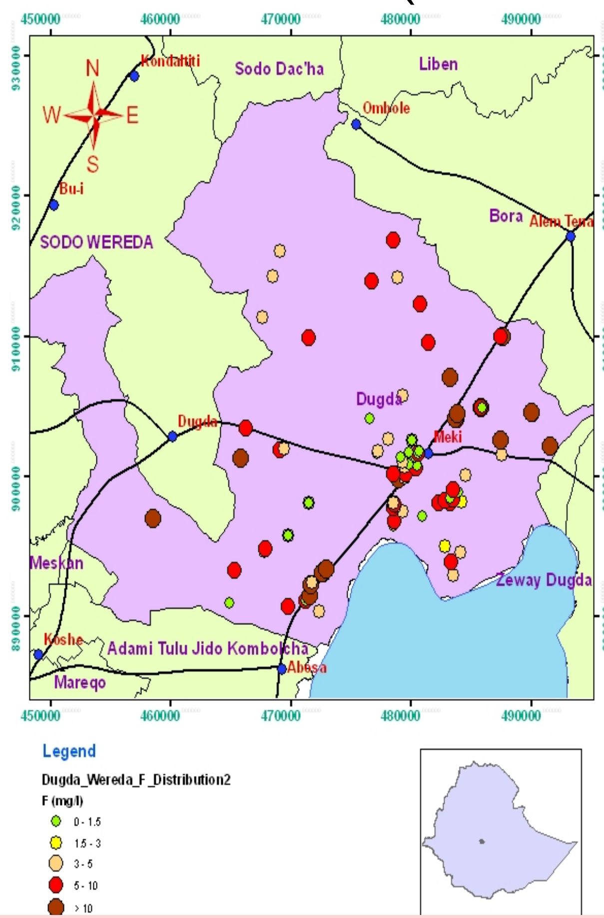
Exposure to high fluoride was low due to the low coverage in the past

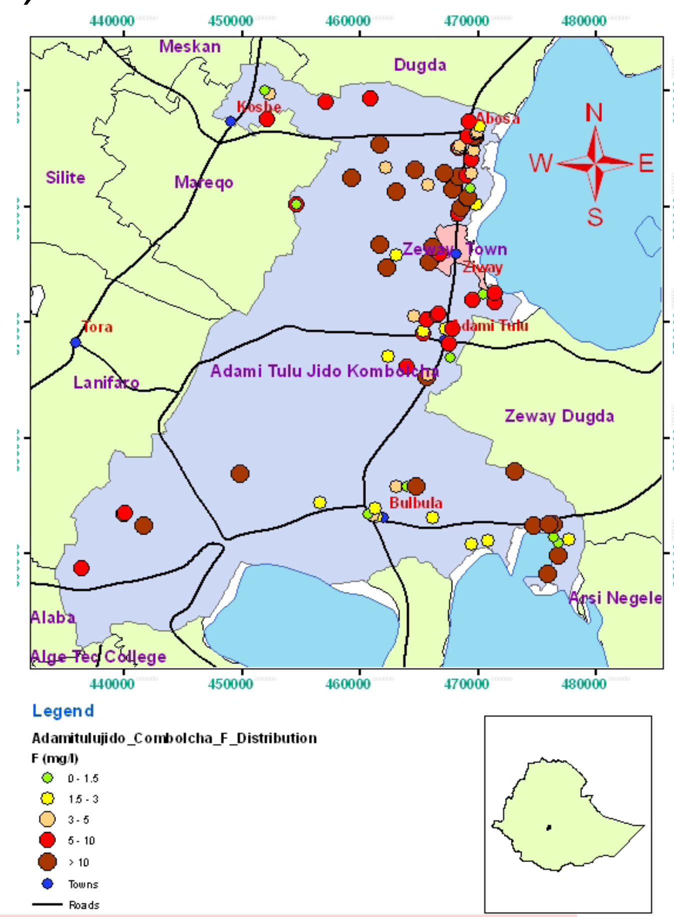
Source: JMP 2010 report

Water Supply Coverage: Ethiopia (Cont'd)

Example: Ground Water Supply sources in High Fluoride Risk Woredas (Districts)







It is impossible to achieve either the MDG or the Government target under such conditions

Water Supply Coverage: Ethiopia (Cont'd)

The proportion of exposure to high fluoride is increasing

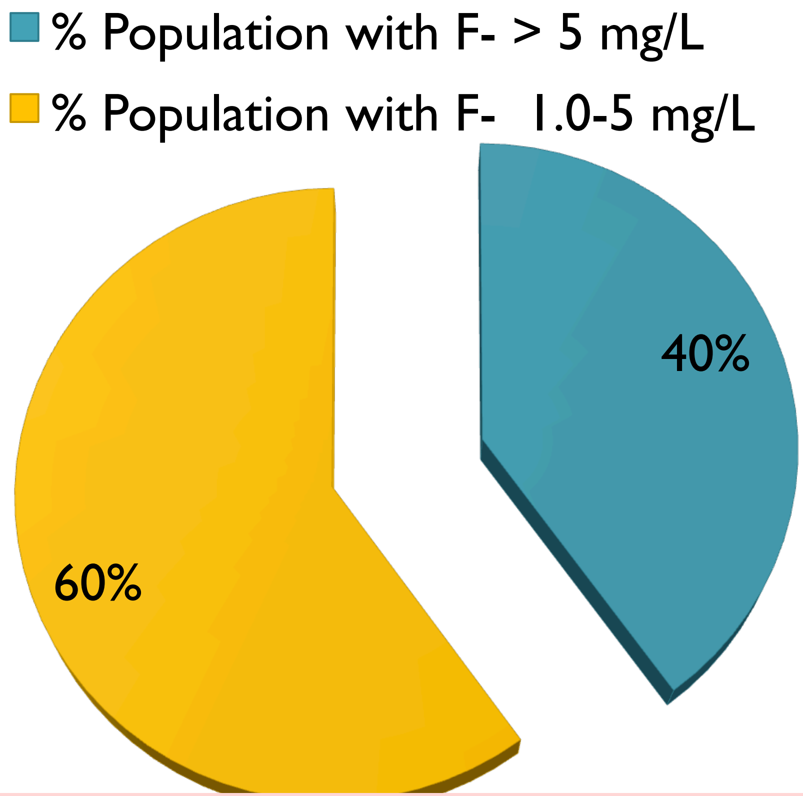


Photo courtesy of Prof. Avner Vengosh, Duke University, USA

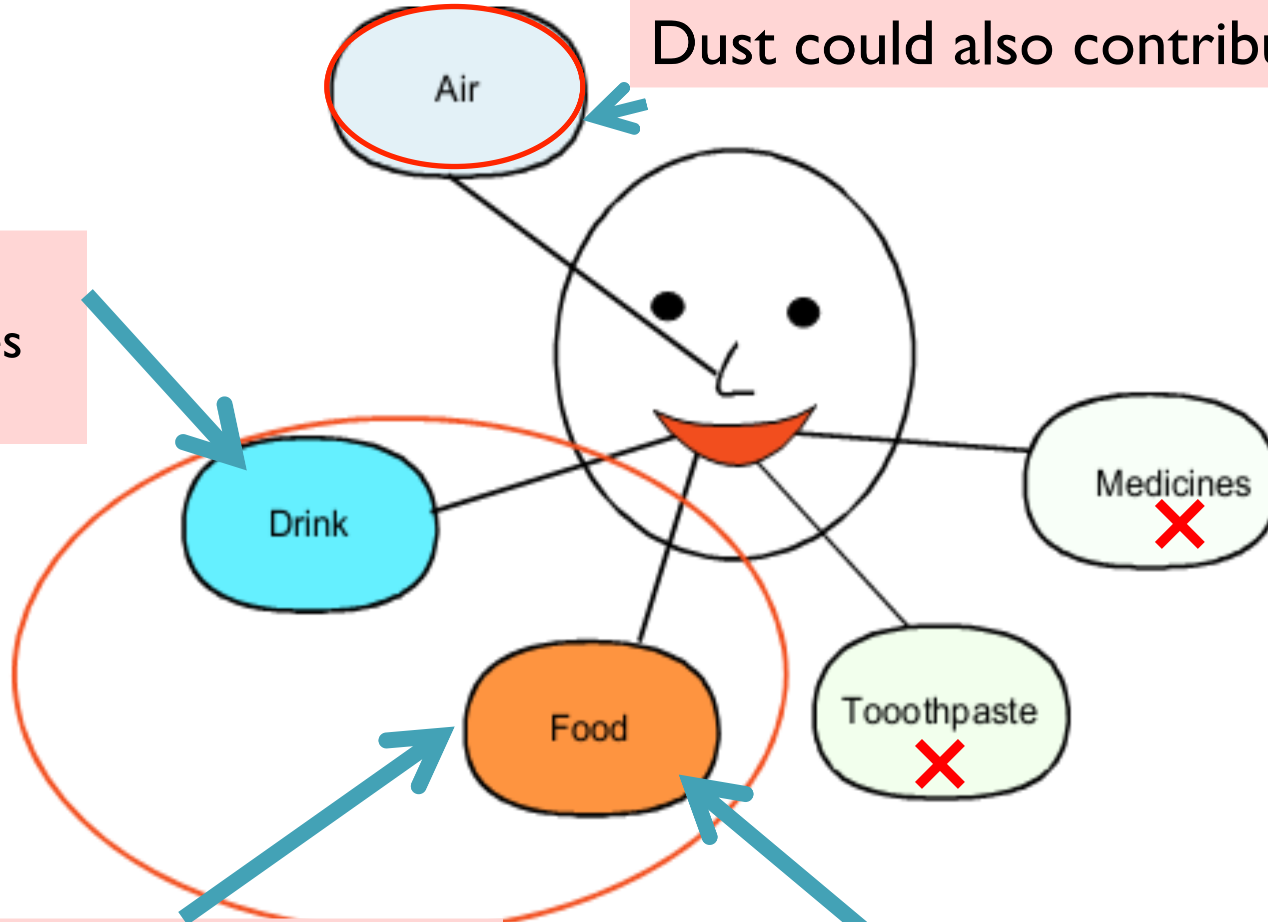
Water supply coverage from groundwater sources has increased, but apart from microbial contamination, other water safety issues have not been addressed

Total Daily Fluoride Intake: Situation in Ethiopia

Drinking Water alone may not be the only cause of fluorosis

Dust could also contribute??

- Drinking water
- Local beverages
- Tea

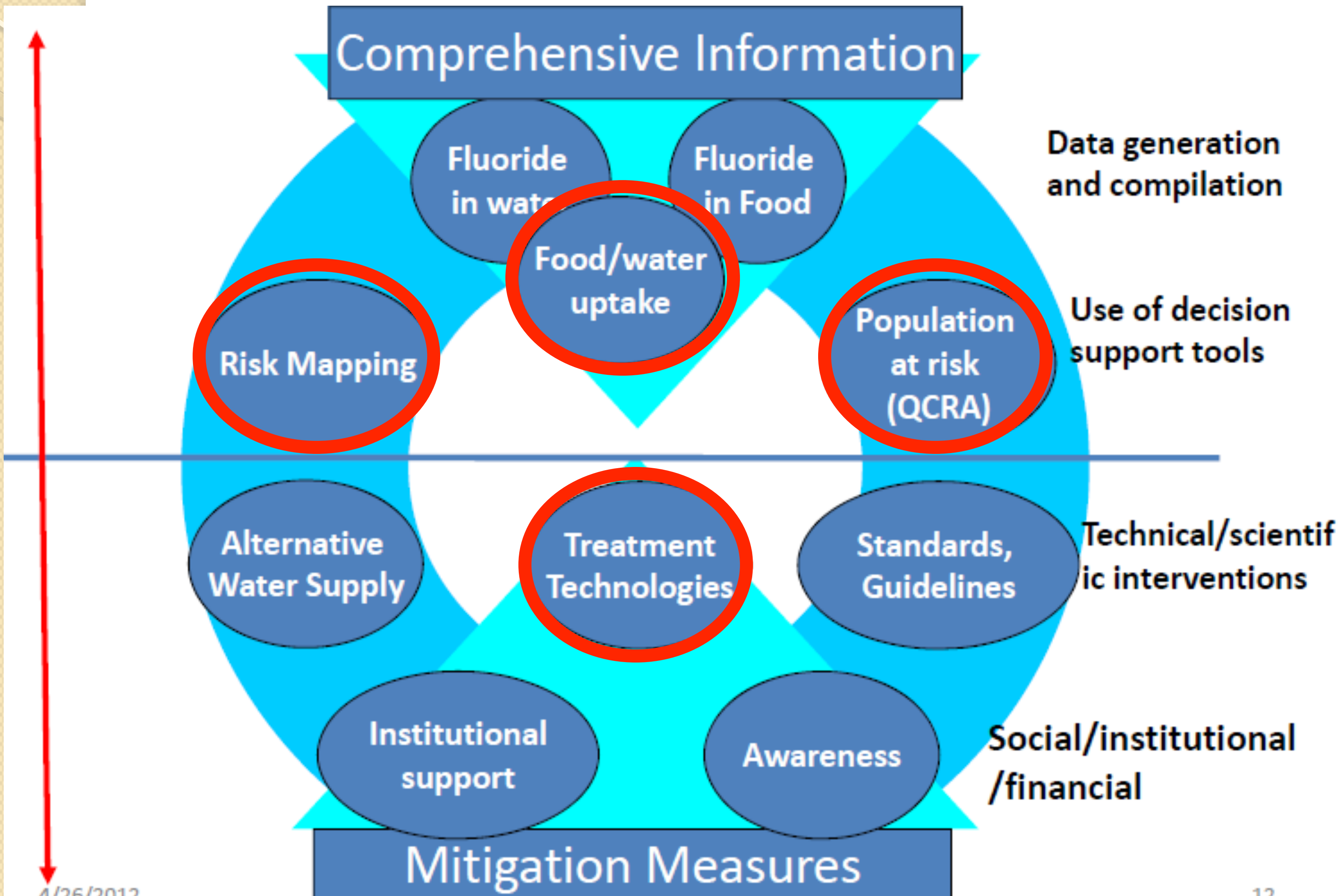


Water is used for food preparations

Food ingredients contain fluoride from soil and water

Integrated Fluorosis Mitigation Framework

Conventional WASH approach may not be applicable to mitigate fluorosis



Dietary Fluoride Intake

Mean Fluoride Content of Common Food Items in Ethiopia

No.	Food Items	Mean Fluoride (mg/kg)
1	**Teff**	**21.9-27**
2	Maize	12.2
3	Wheat	6.8
4	**Red Chili**	**18.8**
5	**Salt**	**27.7**
6	Fish	4.0
7	Coffee	1.75
8	**Green tea bags**	**245-265**
9	**Black tea leaves**	**302-728**
10	**Black tea bags**	**258-300**

2. M. Desalegn and F. Zewge, Toxicological and Environmental Chemistry,

Dietary Fluoride Intake **(Cont'd)**

Fluoride Content Staple Food Item (Teff) in Ethiopia

Sample site	Type of teff	Average F^- in mg/kg
Rift Valley Area	**White teff**	**25.6±0.21**
	Red teff	**21.9±0.06**
	Mixed teff	**26.8±0.02**
Adjacent highland	White teff	19.3±0.26
	Red teff	16.8±0.02
	Mixed teff	17.6±0.01
Far from Rift valley: West	White teff	15.5±0.06
	Red teff	15.3±0.07
	Mixed teff	16.4±0.04
Far from Rift valley: North	White teff	10.5±0.01
	Red teff	9.17±0.04
	Mixed teff	16.7±0.04

Research Question: What is the form of fluorine in food items? Inorganic or Organic ?

Dietary Fluoride Intake (Cont'd)

Fluoride from Water to Cooked Foods

Increase in Fluoride concentration the in water (mg/L)	3-fold	10 -fold
Increase in in fluoride content of prepared food (mg/kg)	1.6 fold	3.5 fold

Levels of fluoride in foods are significantly affected by the fluoride content of the water used in preparation or processing, most notably in beverages and foodstuffs to which water is added prior to consumption or for preparation

Health Impacts of Fluoride in Ethiopia

4. Systemic fluorosis??

4. Crippling fluorosis + Dental

3. Skeletal + Dental Fluorosis

2. Ostesclerosis + Dental F

1. Dental Fluorosis (Mild –Sever)

> 10 mg/L

5- 10 mg/L

>1.0 mg/L

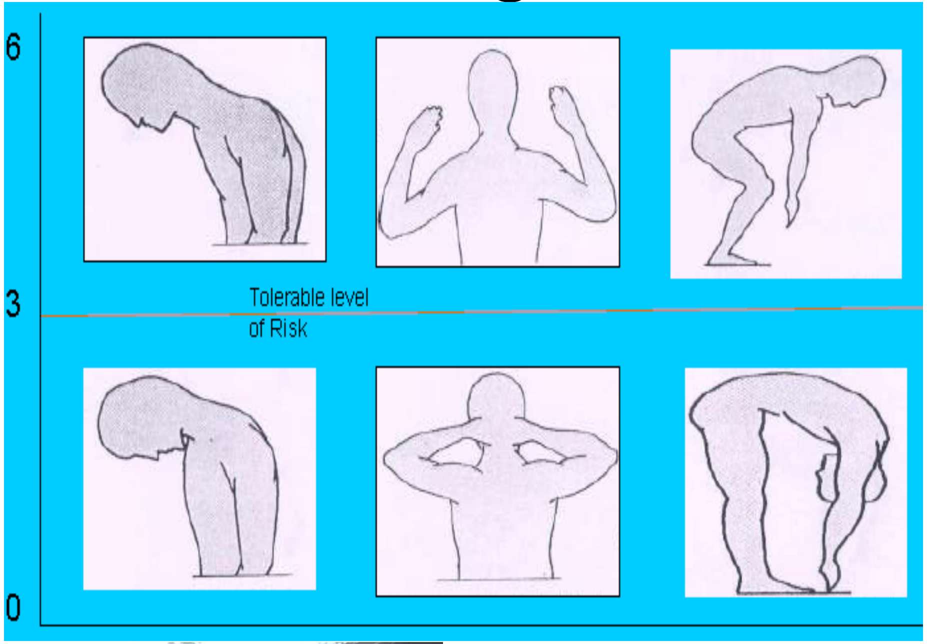
F- in Drinking Water

The over all socio economic and psychological impact due to fluorosis could be tremendous, but not quantified yet

Health Impacts of Fluoride in Ethiopia (Cont'd)

Risk Assessment in Selected Rural Villages

1. **Dental Fluorosis**
   - Deans Index based on Mouse Prevalence
2. **Skeletal Fluorosis**
   - **Physical exercise**
3. **Daily fluoride intake**
   - Sampling and analysis of food and water
   - Household questionnaire



10% of the population in eight villages

Health Impacts of Fluoride in Ethiopia (Cont'd)

Disability Adjusted Life Years (DALYs)

$$DALY = YLL + YLD$$

Where YLL = years of life lost
YLD = years lived with disability

$$YLD = I \times DW \times L$$

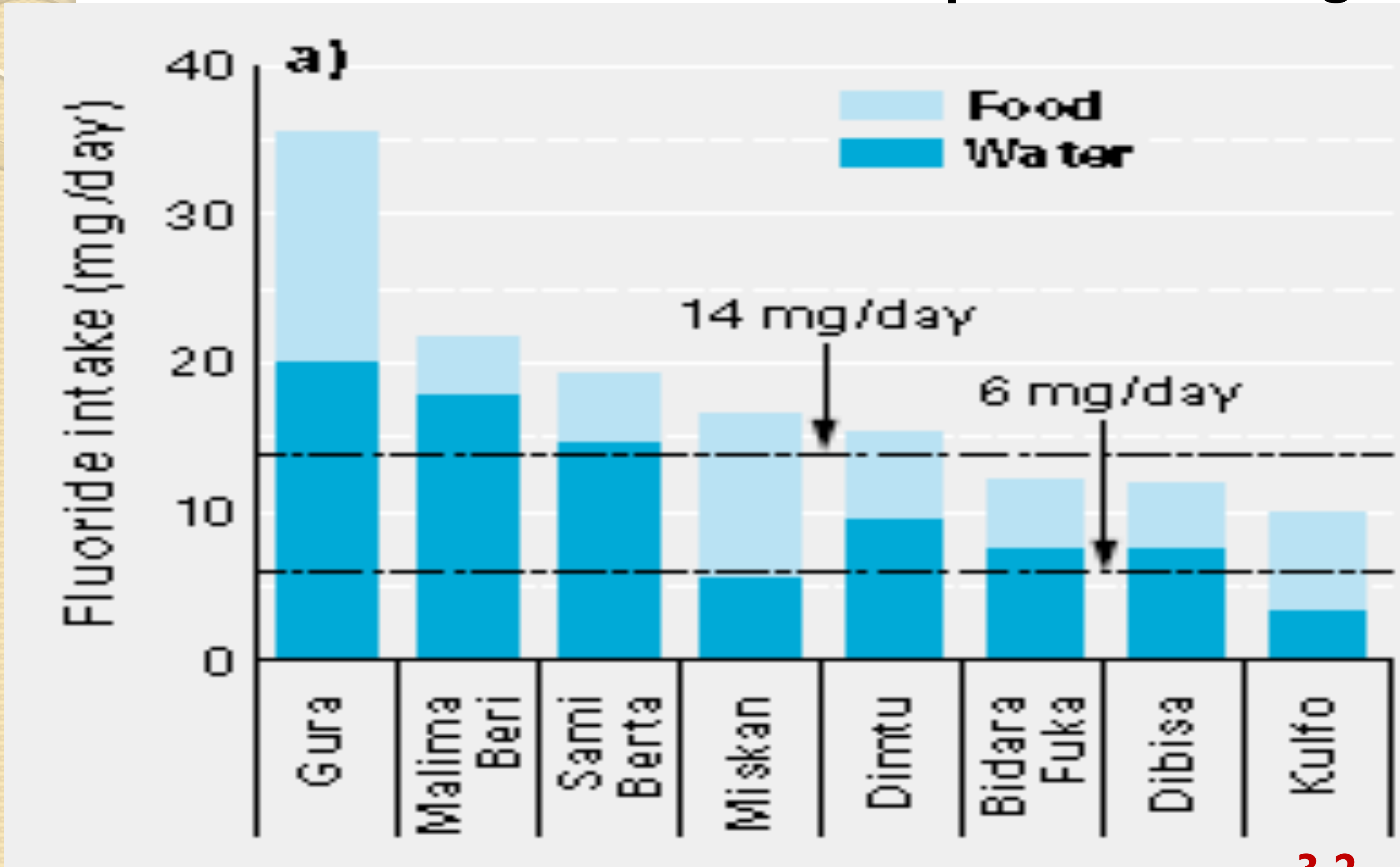
- **It is the health outcome measured with quality of life reduced due to disability.**

One DALY is a health gap measure, equating to one year of healthy life lost.

Where I = number of incident case (field observations)
WD = disability weight (0.3 for skeletal and 0.024 for dental fluorosis)
L = Average duration of the case (disability) until death in year (Life expectancy for Ethiopia)

Health Impacts of Fluoride in Ethiopia **(Cont'd)**

Risk Assessment in Selected Ethiopian Rural Villages

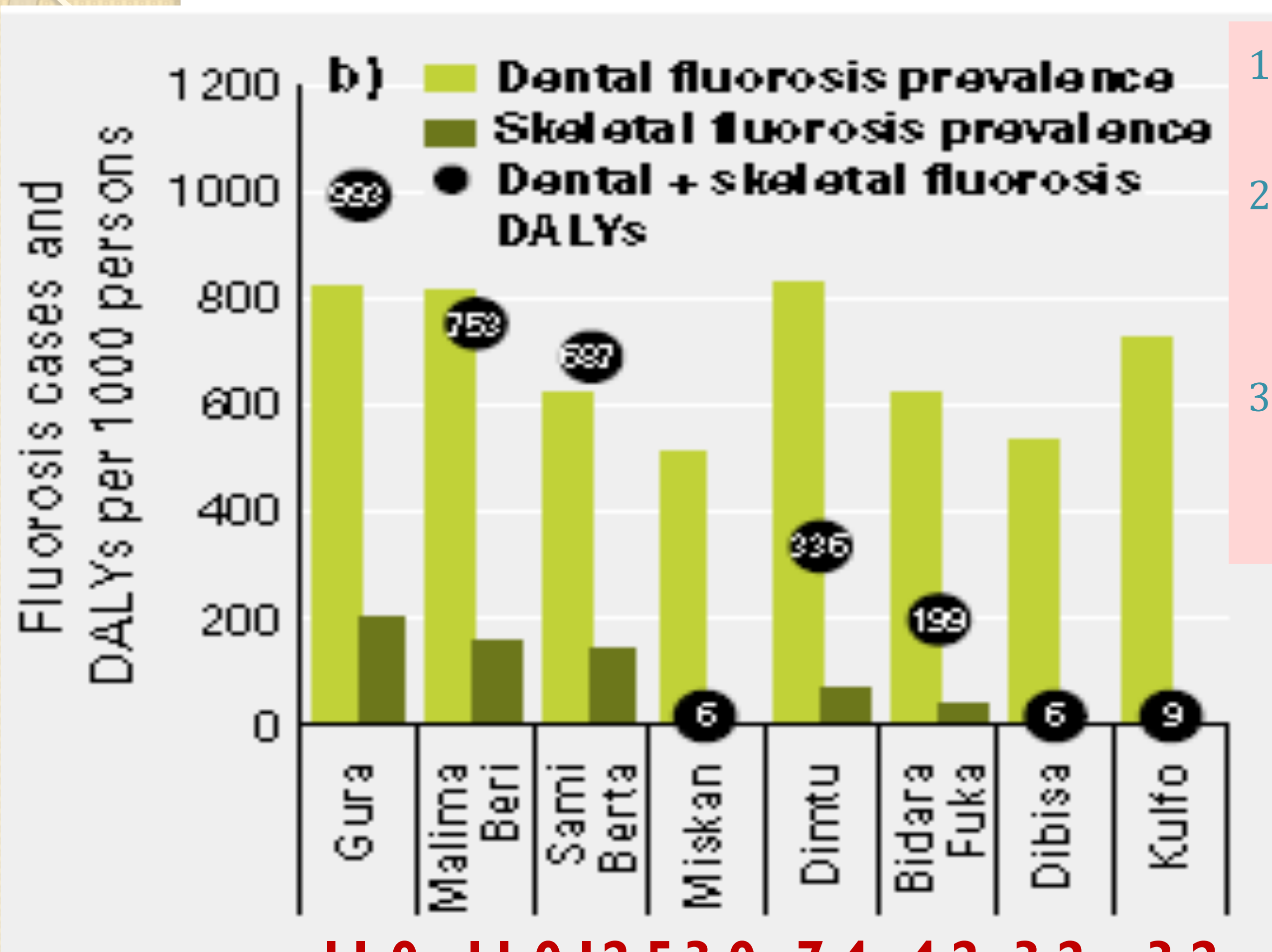


11.0 11.0 12.5 3.0 7.4 4.2 3.2 3.2

Fluoride in Water (mg/L)

Health Impacts of Fluoride in Ethiopia **(Cont'd)**

Prevalence of Fluorosis and DALYs



11.0 11.0 12.5 3.0 7.4 4.2 3.2 3.2

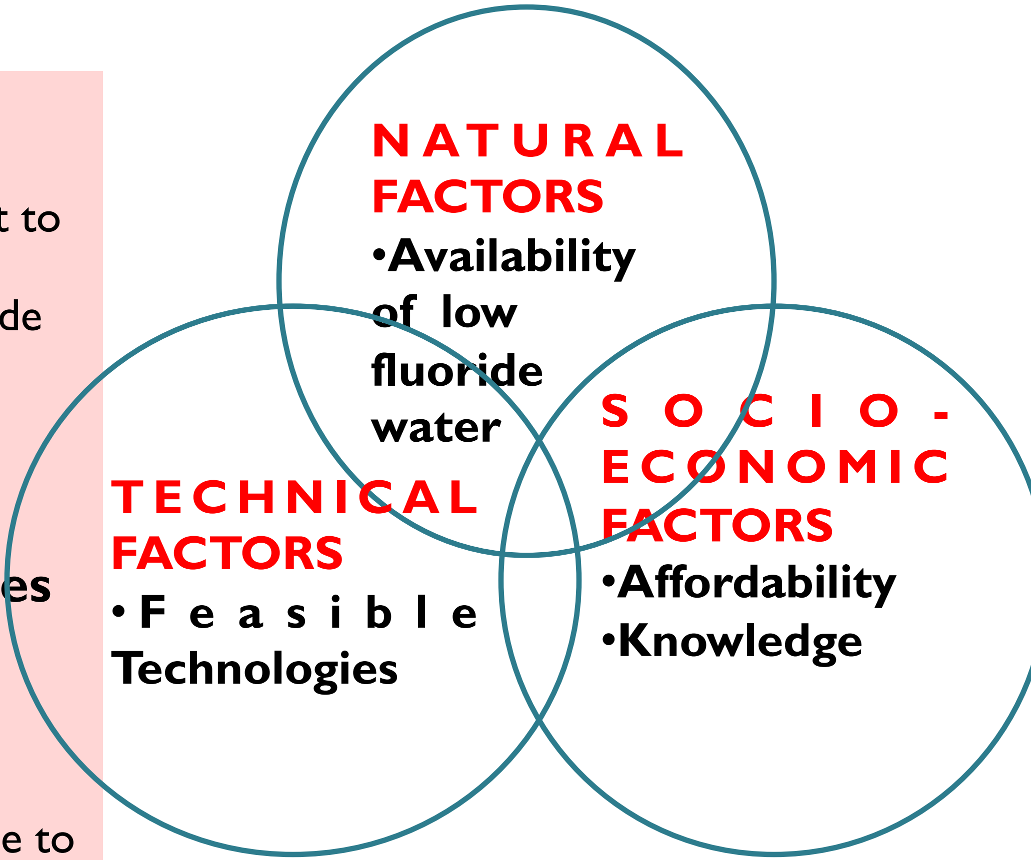
Fluoride in Water (mg/L)

1. SF: above 6 mg/day,
2. Clear excess risk of SF

   14 mg/day.
3. DF and SF are associated with Total Daily Fluoride Intake

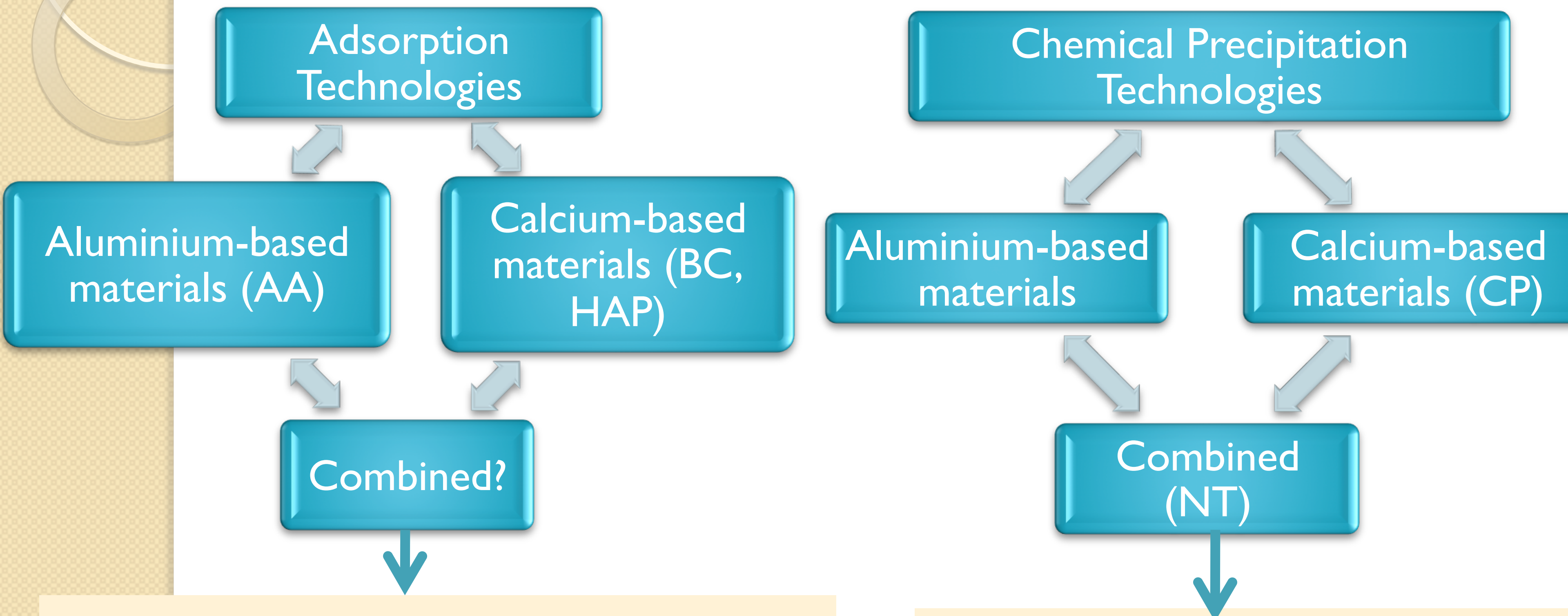
Fluorosis Mitigation Options

1. **Alternative sourcing**
   - Rivers (very few)
   - Rain water harvesting (not sufficient to meet the demand)
   - Groundwater (search for low fluoride water)
2. **Nutritional intervention**
   - Difficult to implement (if not impossible)
3. **Fluoride removal technologies**
   - Membrane Technologies (Very high cost)
   - Chemical precipitation (poor performance)
   - Adsorption/ion exchange (costly due to low capacity)



Defluoridation Technologies

Available Fluoride Removal Technologies in Ethiopia

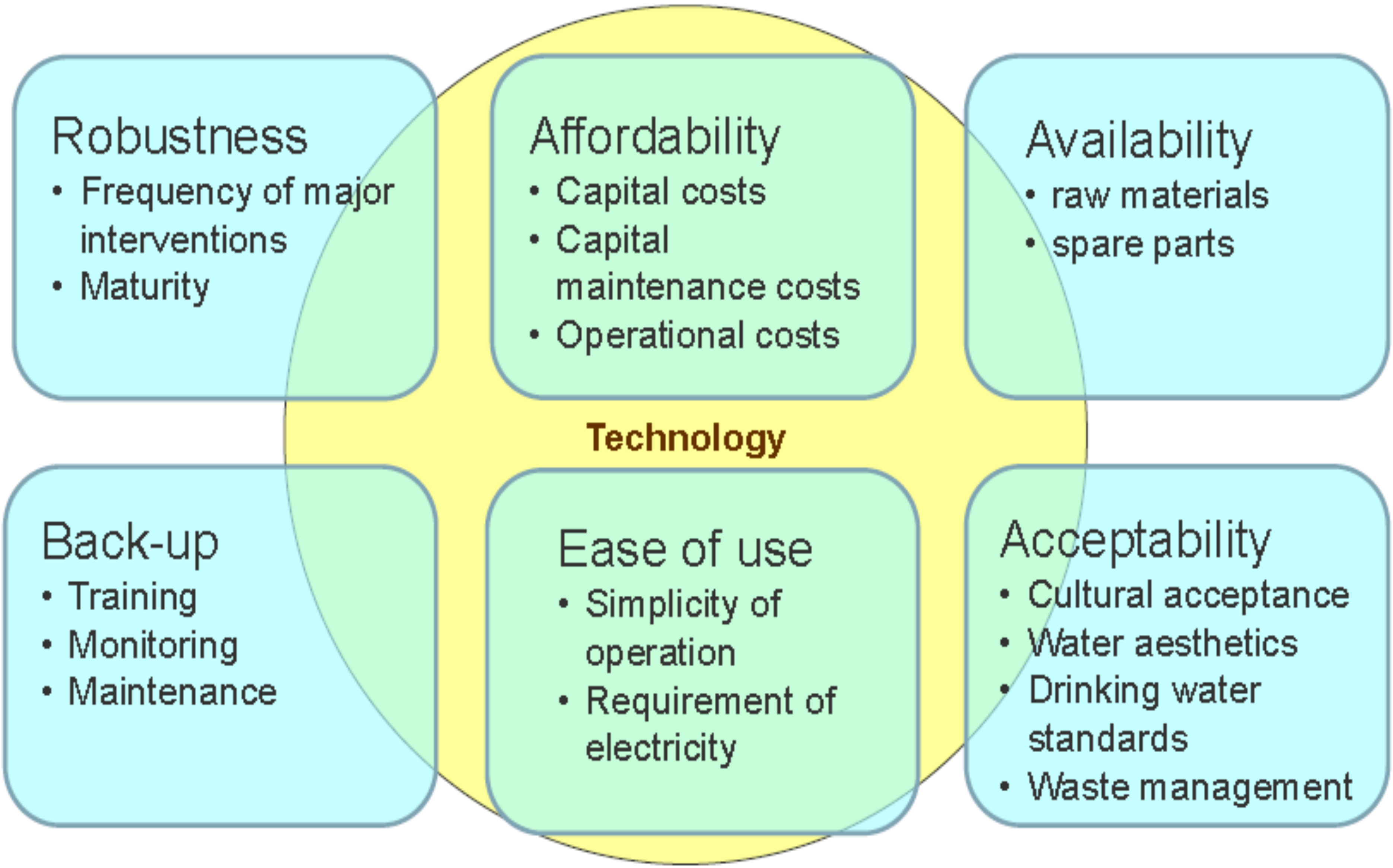


1. Low fluoride uptake capacity per unit mass of material
2. Slow reaction kinetics
3. High operational cost
4. Limited acceptability by users (some)

1. High dosage of chemicals
2. Slow reaction kinetics
3. Low efficiency
4. Sludge handling problem
5. Change the water quality

Defluoridation Technologies (Cont'd)

Sustainability Issues



Defluoridation Technologies (Cont'd)

We are developing High Capacity Fluoride Adsorption Materials

1. Alumnium Hydroxide (AO): Heat treated at 300 °C
2. Aluminium Oxide-Hydroxide (Nano particles)
3. Composite Oxides: Alumimum Oxide/Manganese Oxide
4. Coated high surface area materials

The Most Important Properties for Suitable Adsorption Materials

1. Specific Surface area
   – Depends on how the material is synthesized
2. Surface chemistry
   – Mainly pH-dependent
3. Material stability
   – Chemical structure

Defluoridation Technologies (Cont’d)

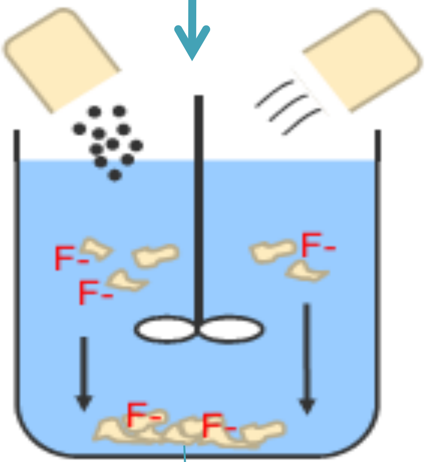
New Fluoride Removal Technologies (AO-Based Technologies)

1) AO-Granules

2) AO-Powder with coagulants

3) AO-Coated on high surface area substrate

4) Composite oxides



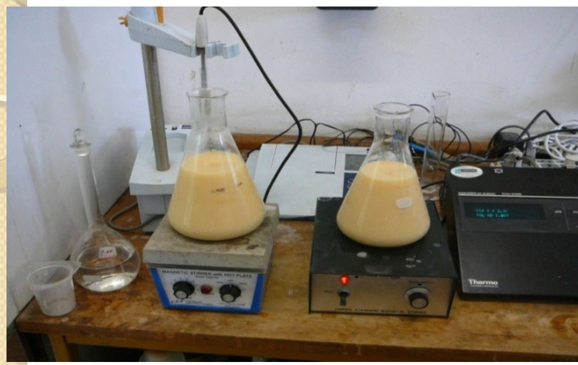
New ongoing collaborative research projects AAU/UO funded by NSF/ USAID

AO-Process

AO-NT Process

Defluoridation Technologies (Cont'd)

Laboratory Synthesis of AO



Synthesis

Filter cake

Sun dried

Furnace 300 °C, 1 hr

AO AA PBE

Defluoridation Technologies (Cont'd)

Characterization of AO Material

1. The elemental composition
   - ICP-OES, ICP-MS, IC
2. The absolute density
   - Pycnometer
3. The surface area
   - N_2 adsorption method
4. The mineral type(s)
   - X-ray diffractometer
5. Surface morphology and particles
   - Scanning electron microscopy (SEM)
6. The point of zero charge (PZC)

   zeta potential method
7. Chemical Structure and geometry

   ^{27}Al MAS NMR Spectrometer
8. Weight and mineral phase changes upon heating
   - Thermo gravimetric Analysis (TGA)
9. Solid surface acidity
   - Auto surface titration apparatus
10. Material stability test as a function of pH

Defluoridation Technologies (Cont'd)

Surface Properties and Fluoride Removal

Material	Density, g/cm^3	Surface area m^2/g	Acidity, meq/g	Fluoride uptake, mg/g	Rxn time (h)
Activated alumina (AA) (Compalox^R AN/V-812), Germany	**3.48-3.97**	250	-0.24	1.75	6
Extrudated Pseudoboehmite (PBE), Germany	3.01	300	-0.23	0.94	10
AO	**2.47**	**38**	**1.8**	**23.7**	**1**
Nano aluminium oxide-hydroxide	**2.18**	**-**	**-**	**20.7**	**0.5**
AO/Manganese oxide	**2.78**	**12.7**	**-**	**4.5**	**2**

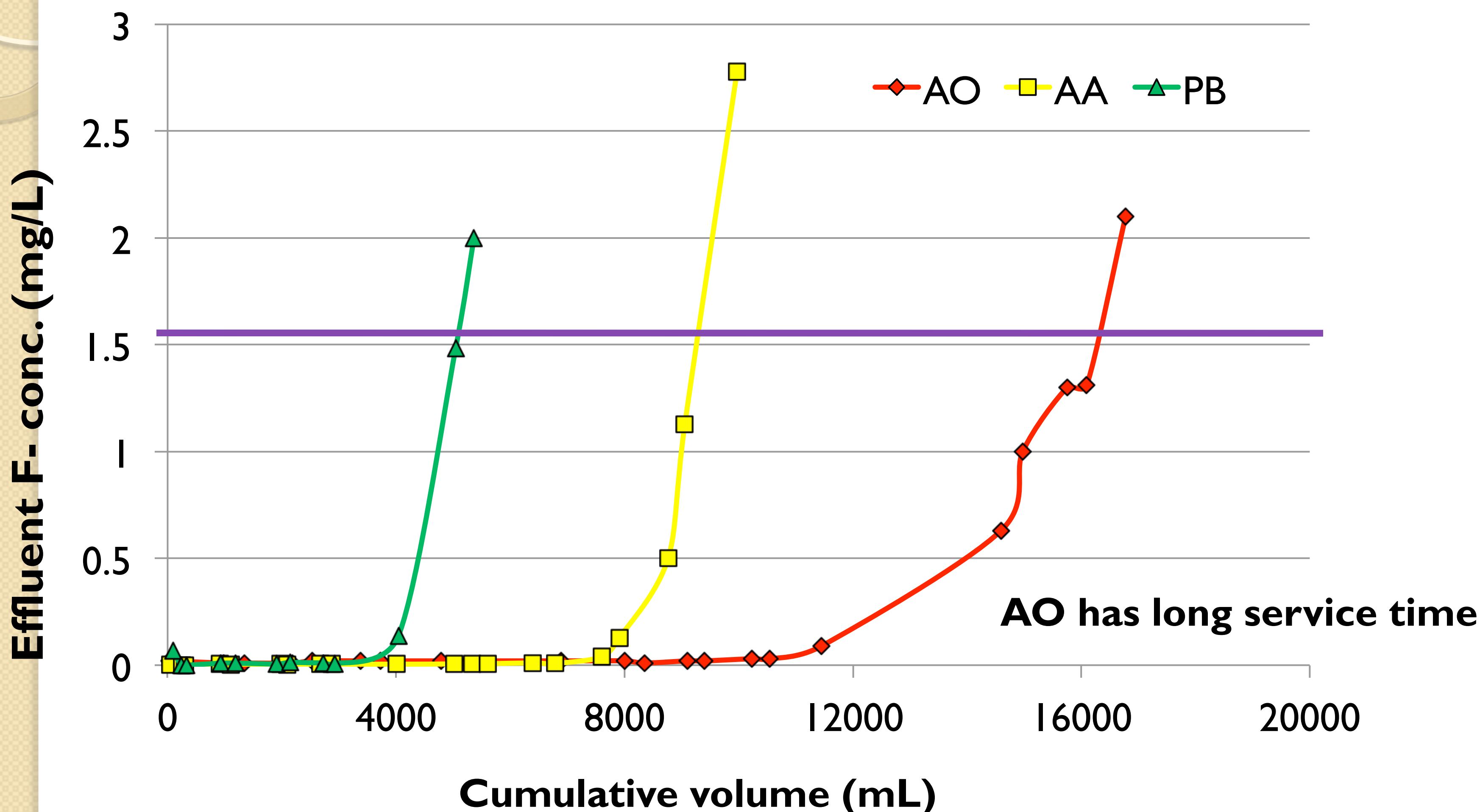
The AO material :
$Al_4(SO_4)(OH)_{10}$

AO AA

PBE

Defluoridation Technologies (Cont'd)

Comparison of Fluoride breakthrough (Service time) of packed bed columns



AO (♦), AA (■) and PB (▲) at influent fluoride concentration (20 mg/L) and flow rate (10 eBV/day).

Defluoridation Technologies (Cont'd)

Pilot scale production of AO: Simple processing

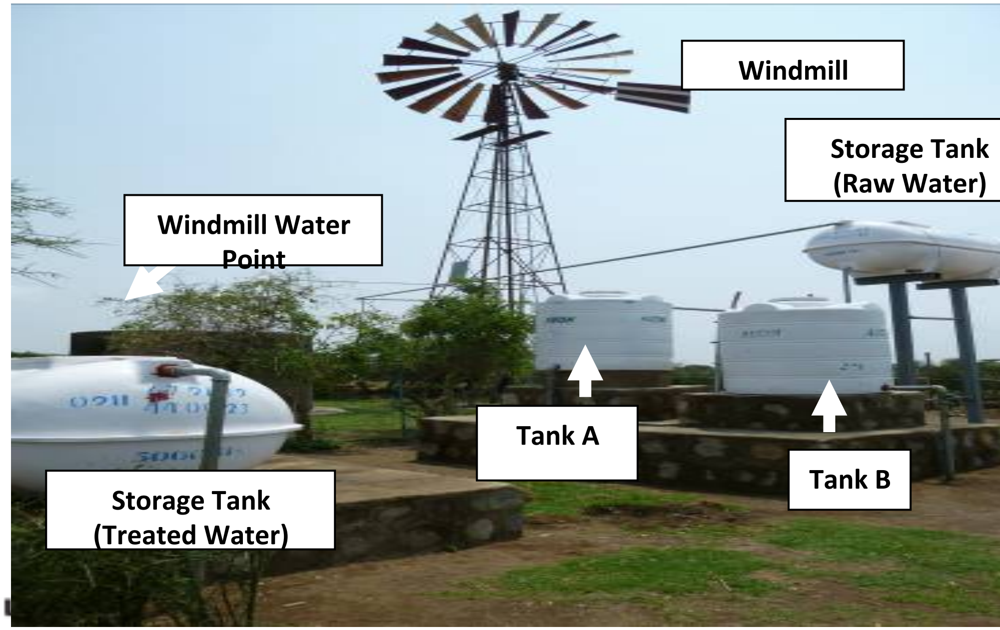
- Optimizing synthesis conditions
- Filtration and washing
- Drying of the Filter Cake
- Calcination at 300 °C
- Crushing and Sieving

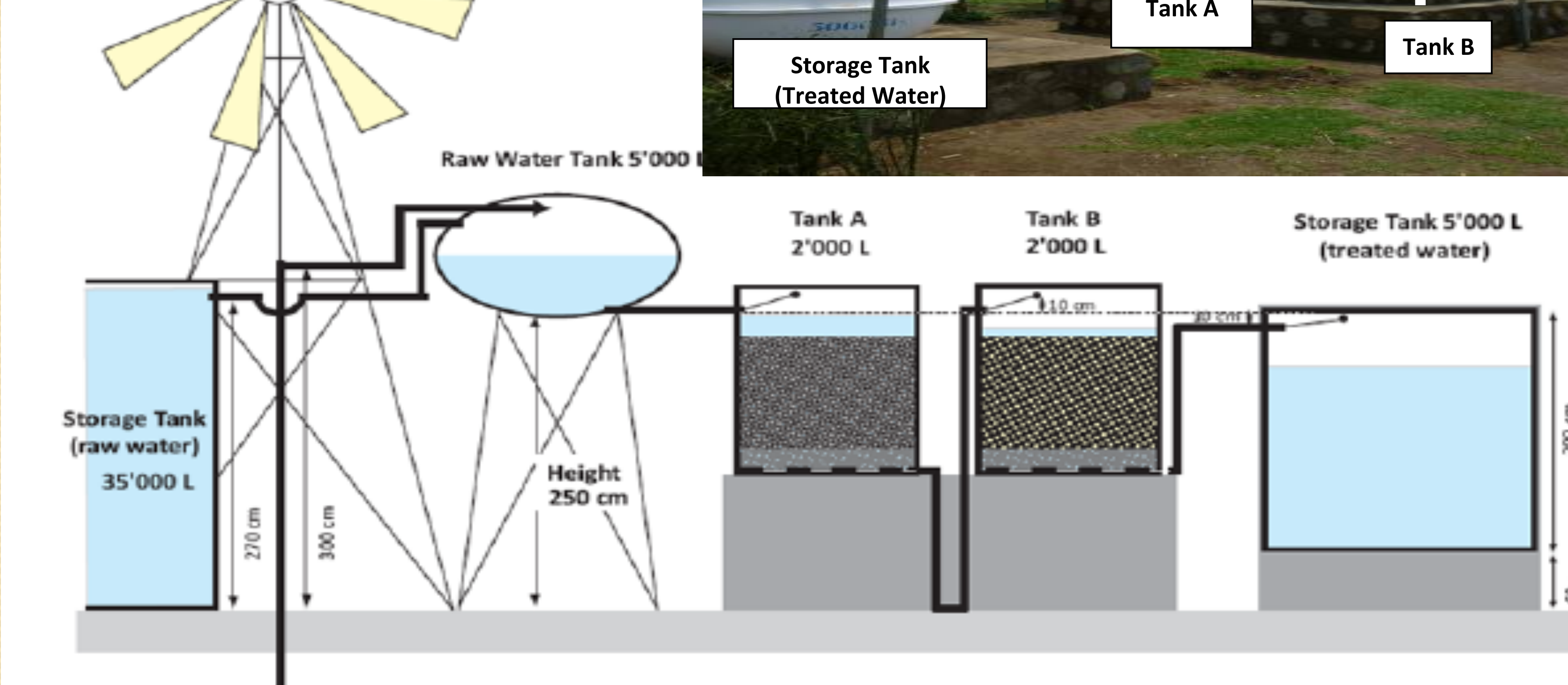
- Granules
  - Used in packed bed column

- Fine powder
  - Used in a combined Nalgonda -AO process

Defluoridation Technologies **(Cont'd)**

AO community Filter in a Rural Village





Defluoridation Technologies (Cont'd)

AO community Filter Performance

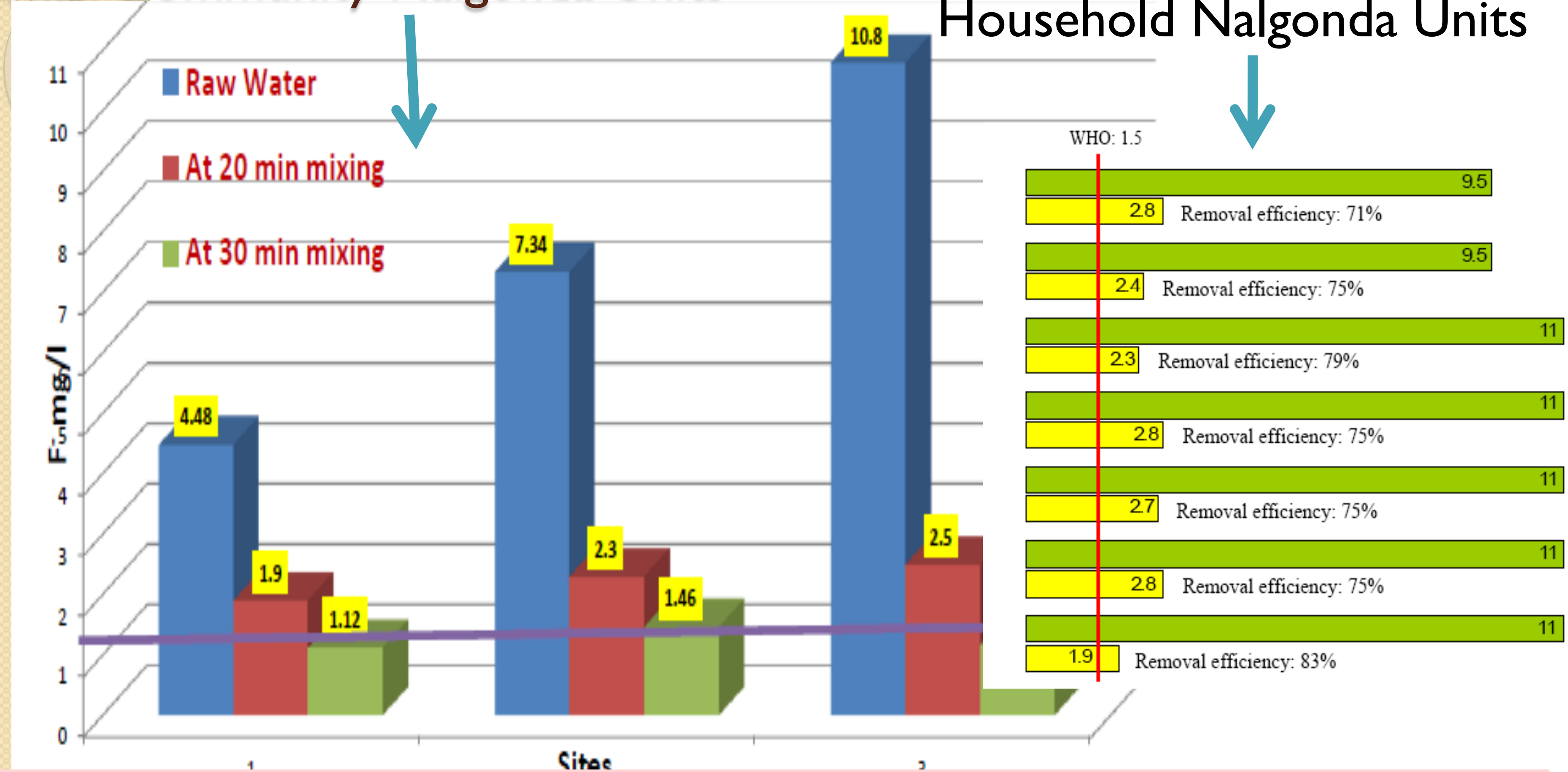
Constituents	Raw water (mg/L)	Treated water (mg/L)
Fluoride	8.1-10.1	0.01-1.52
Sulfate	7.1-9.5	69.1-1006.3
Chloride	63.4-67.7	61.9-68.2
Aluminium	$(4.9\text{-}18.2) \times 10^{-3}$	$(12.8\text{-}59.4) \times 10^{-3}$
Sodium	278.0-295.5	283.3-336.0
Iron	1.77-2.56	1.85-2.62
Calcium	29.5-33.1	22.3-71.5
Silicon	29.7-30.8	1.7-4.4
Magnesium	6.8-7.3	5.9-9.2
Arsenic	$(1.3\text{-}5.1) \times 10^{-3}$	$(0.2\text{-}0.4) \times 10^{-3}$
Uranium	$(1.3\text{-}1.8) \times 10^{-3}$	$(0.1\text{-}0.3) \times 10^{-3}$
Selenium	$(2.9\text{-}5.1) \times 10^{-3}$	$(0.1\text{-}0.8) \times 10^{-3}$
pH	7.84-8.23	6.68-8.30

WHO guideline, As (10 ug/L); U (15 ug/L); Se (10 ug/L)

Defluoridation Technologies (Cont'd)

Small Community Nalgonda Units

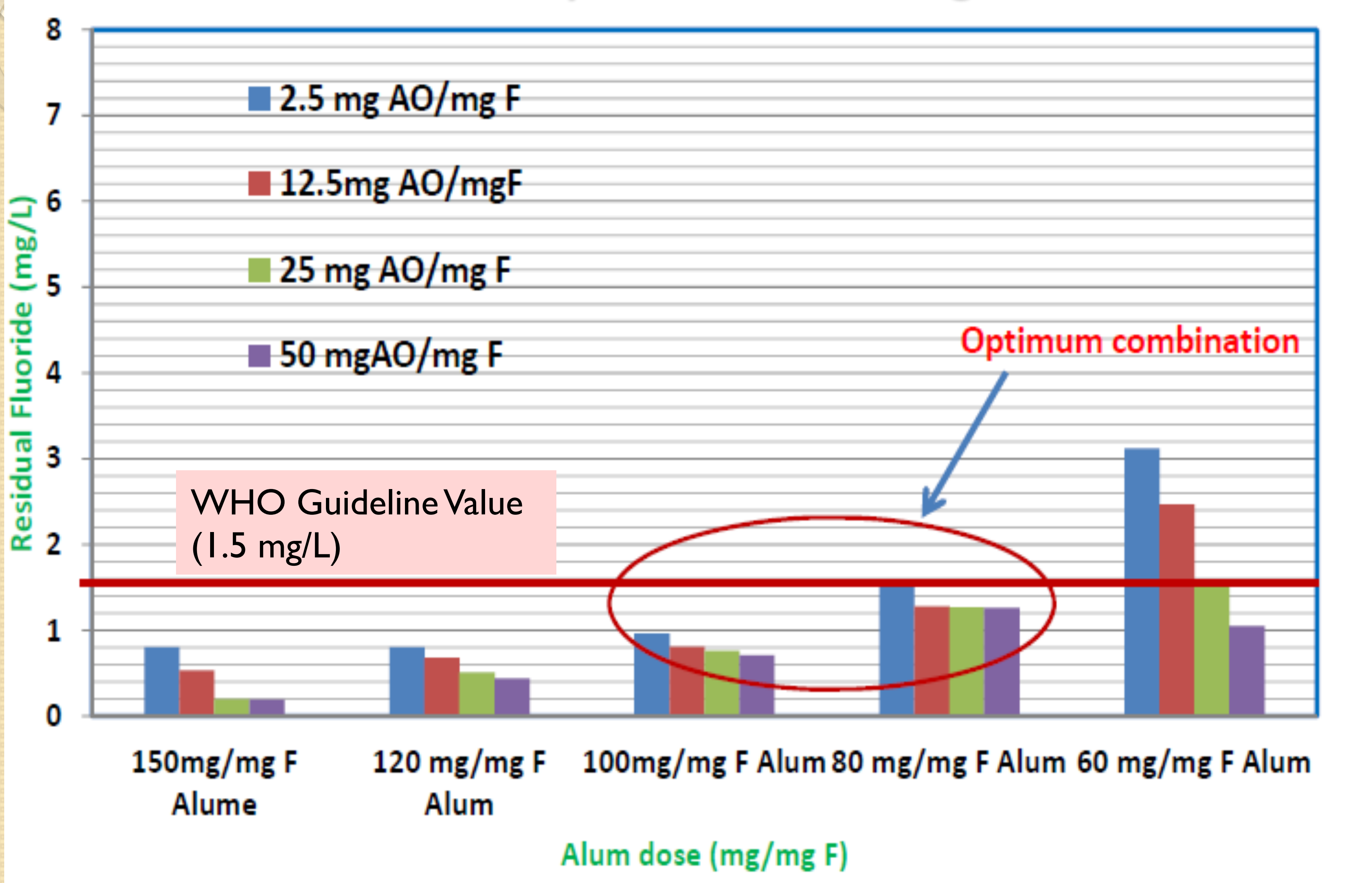
Household Nalgonda Units



1. **Not effective for raw water fluoride concentration exceeding 10 mg/L**
2. **Alum dose: 150 – 170mg/mg of fluoride and lime dose: 35 – 40% of alum which result in large amount of sludge**
3. **The treatment efficiency is limited to about 70% in most cases**

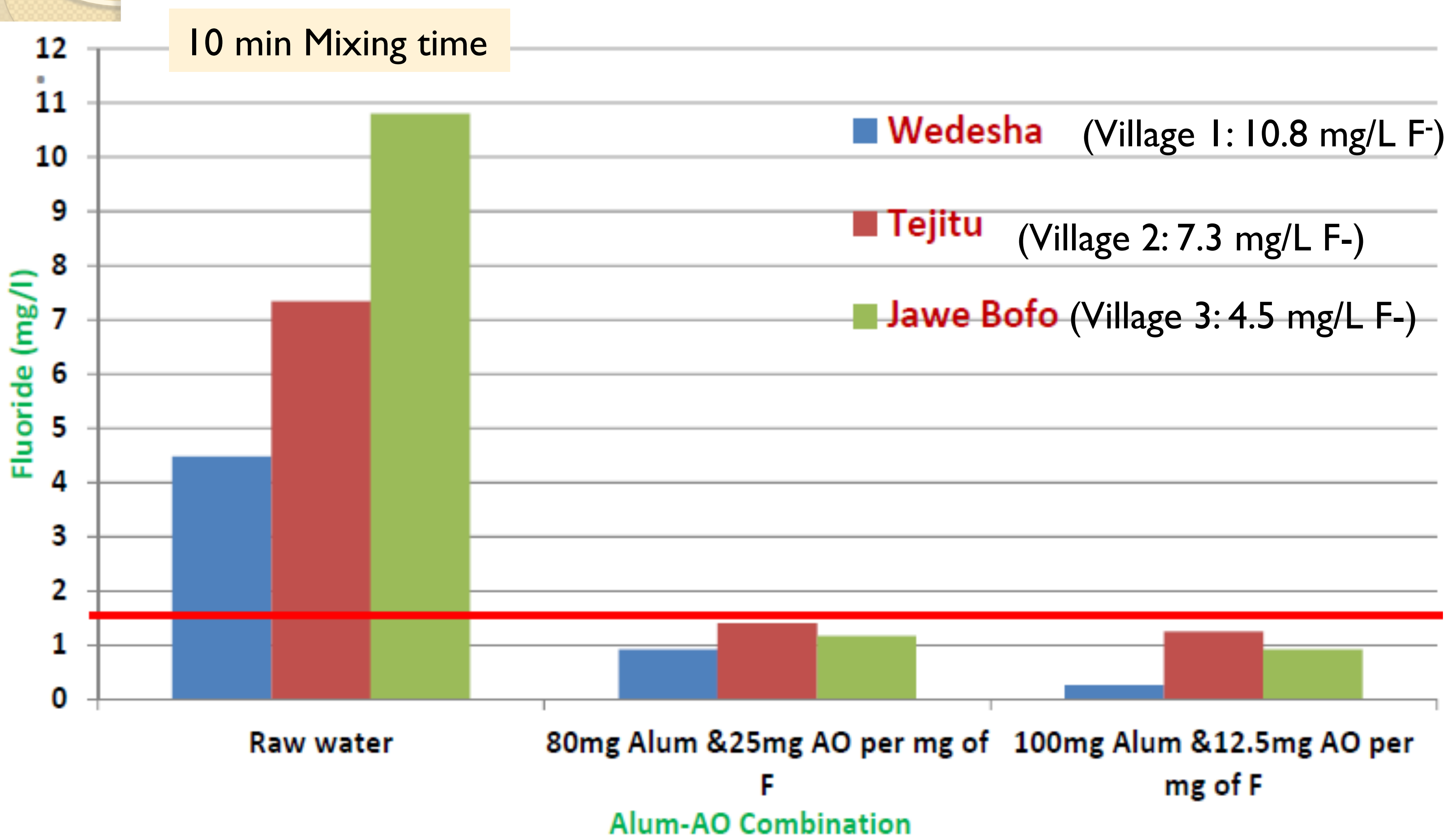
Defluoridation Technologies (Cont'd)

Fluoride Removal by Combined Nalgonda-AO Process



Defluoridation Technologies (Cont'd)

Performance of Rift Valley Villages



Application of AO-NT to Household Water Treatment

- The main advantage of the Nalgonda-AO Process is application atHousehold level
  - **About 20 g of alum + 2.5 g AO would be sufficient to treat 20 L water containing 10 mg/L of fluoride**

  [25.5 g 9(Alum +AO + Lime)]
  - **It can be prepared to remove bacteria and other trace metals as well**
- Estimated chemical cost is about (0.5 USD/m^3)

Concluding Remarks

1. High fluoride in groundwater seriously is affecting water availability and access to safe water
2. Effective mitigation of fluorosis can only be achieved if total daily fluoride intake could be minimized
3. Detailed hydrological and hydro geological studies will be required to identify groundwater resources with low fluoride
4. Through intervention of appropriate technology and a community-based business model, the fluoride problem has the potential to be transformed into an opportunity in remote communities
5. It is essential to ensure community ownership/ leadership of mitigation measures throug**h** **e**ffective awareness programs

Acknowledgements

- Ministry of Water and Energy
- UNICEF Ethiopia
- WHO Ethiopia Country Office
- Addis Ababa University
- Swiss federal Institute of Aquatic Science and Technology (Eawag)
- The University of Oklahoma

Thank You!

UN resolution 64/292, recognizes "the right to safe drinking water and sanitation as a human right that is essential for the full enjoyment of life and all human rights"

Additional slides

The Most Important Properties for Suitable Adsorption Materials

1. Specific Surface area
   - Depends on how the material is synthesized
2. Surface chemistry
   - Mainly pH-dependent
3. Material stability
   - Chemical structure

- Aluminium hydroxides
  - Crystalline
    - Trihydroxides
      - Gibbsite (β- aluminium hydroxide)
      - Bayerite(α- aluminium hydroxide)
      - Nordstrandite (γ - aluminium trihydroxide)
    - **Oxide-hydroxides**
      - **Boehmite (γ -aluminium trioxide)**
      - Diaspore (α -aluminium oxide hydroxide)
  - Gelatinous
    - **Amorphous**
    - Pseudo-boehmite

Defluoridation Technologies (Cont'd)

Pilot scale production of AO: Simple processing

Aluminium Sulfate, 10.2 Birr/Kg

+

Caustic Soda, 20 Birr/Kg

Mixing

These steps can be easily scaled up and automated

Filtration and washing

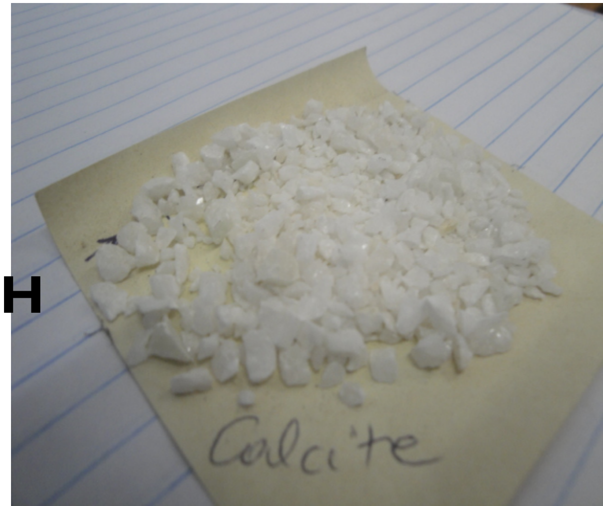
Filter cake

Defluoridation Technologies (Cont'd)

Calcination at 300 °C , Crushing and Sieving

The required product with defined particle size range (1-2 mm)

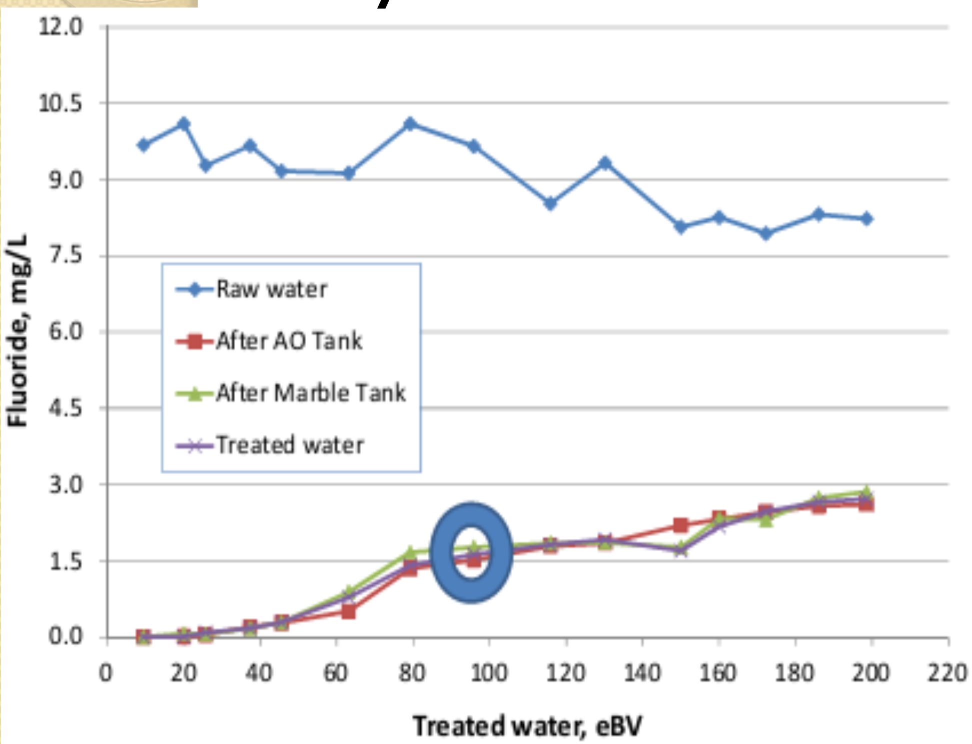
Marble chips to control pH



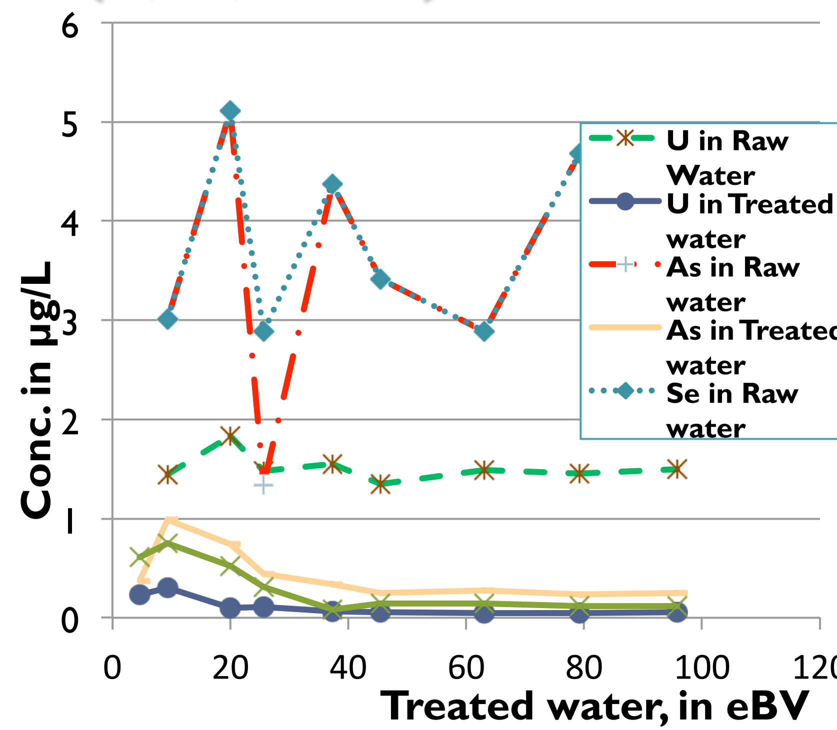
Defluoridation Technologies (Cont'd)

AO community Filter Performance

Fluoride removal performance of community filter



Uptake of Other Contaminant Ions (U, As, and Se)



WHO guideline, As (10 ug/L); U (15 ug/L); Se (10 ug/L)

Defluoridation Technologies (Cont'd)

Comparison of Fluoride Uptake Capacity and Rates of Aluminium Oxide-Based Adsorbents

Adsorbents	Adsorption capacity(mg/g)	Equilibrium time (h)	References
Activated alumina (grade: A-25)	1.78	6	Ghorai and Pant, 2005
Activated alumina (grade: AD101-F)	0.4	10	Maliyekkal et al., 2006
AO	23.7	1	Our Study (Beneberu et al., 2006)
MOAO	4.5	2	Our study
Nano AlO(OH)	20.7	0.5	Our study

Defluoridation Technologies (Cont'd)

solid acidity of 1.80 meq/g and surface site concentration of 0.52 meq/g which makes it superior in terms of fluoride uptake compared to all commercially available adsorbents for fluoride removal

Sample	% Al as $Al(OH)_3$	% Fe as Fe_2O_3	% SO_4^{2-}	Total %	PZC
AO	78.3	2.2	19.4	99.9	9.60

XRD : amorphous

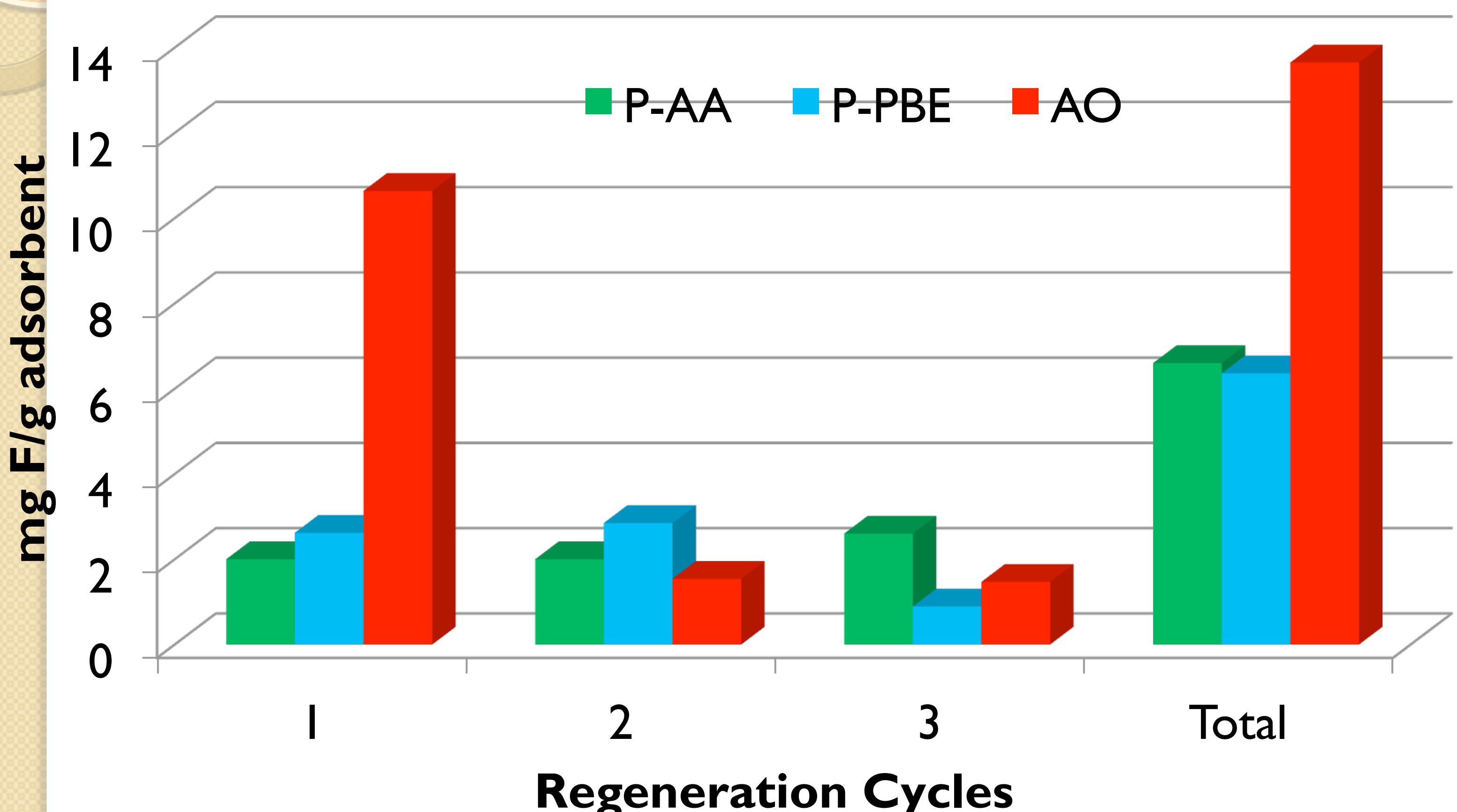
SEM: nano particles (200-300 nm)

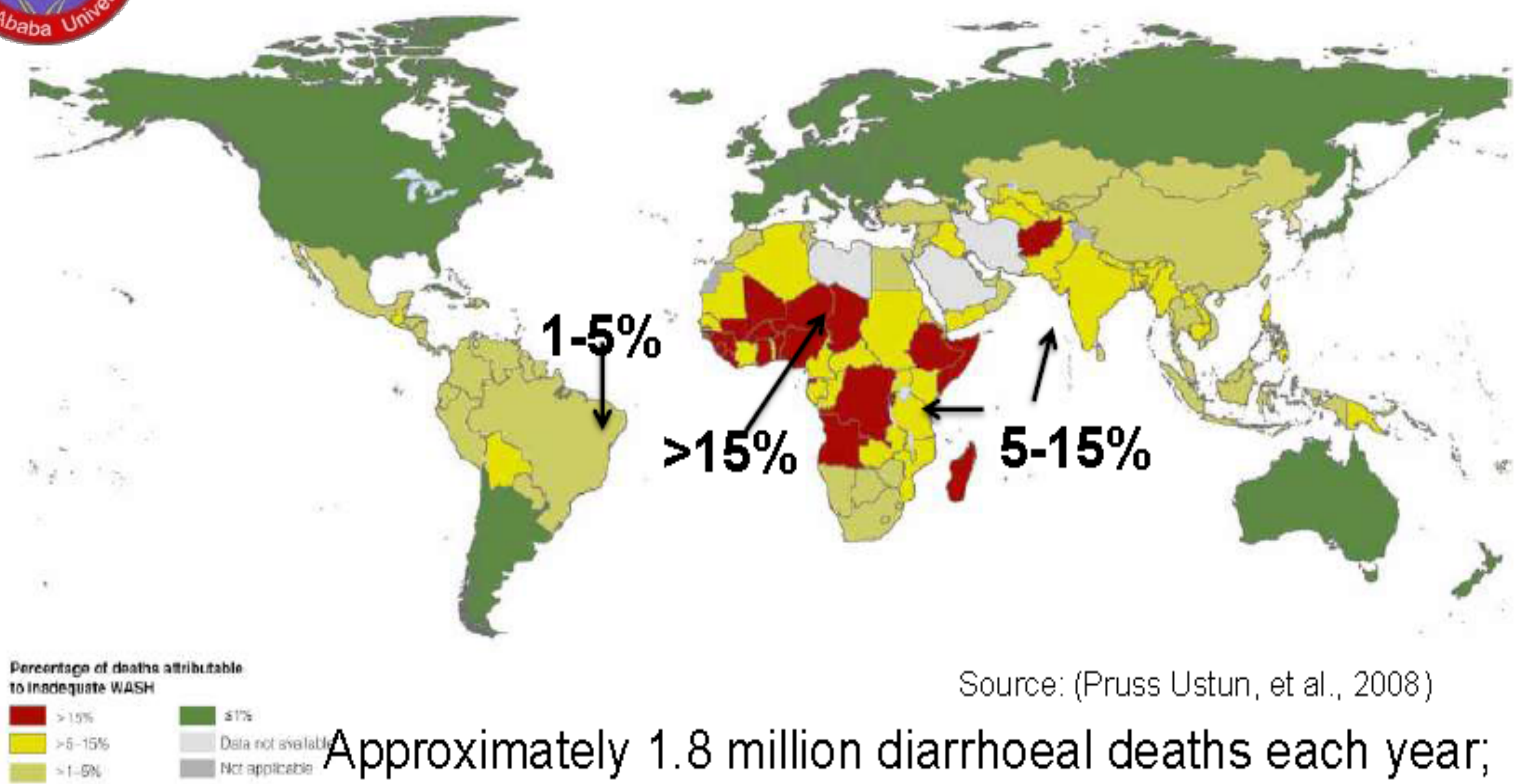
^{27}Al MAS NMR spectra: mixture of tetrahedral and octahedral structure

The AO material might be formulated as: $Al_4(SO_4)(OH)_{10}$

Defluoridation Technologies (Cont'd)

Comparison of Regeneration and Reuse





Source: (Pruss Ustun, et al., 2008)

Approximately 1.8 million diarrhoeal deaths each year; large proportion due to unsafe drinking-water, sanitation and hygiene (2013; WHO).

UN resolution 64/292, recognizes "the right to safe drinking water and sanitation as a human right that is essential for the full enjoyment of life and all human rights"

Dietary Fluoride Intake (Cont'd)

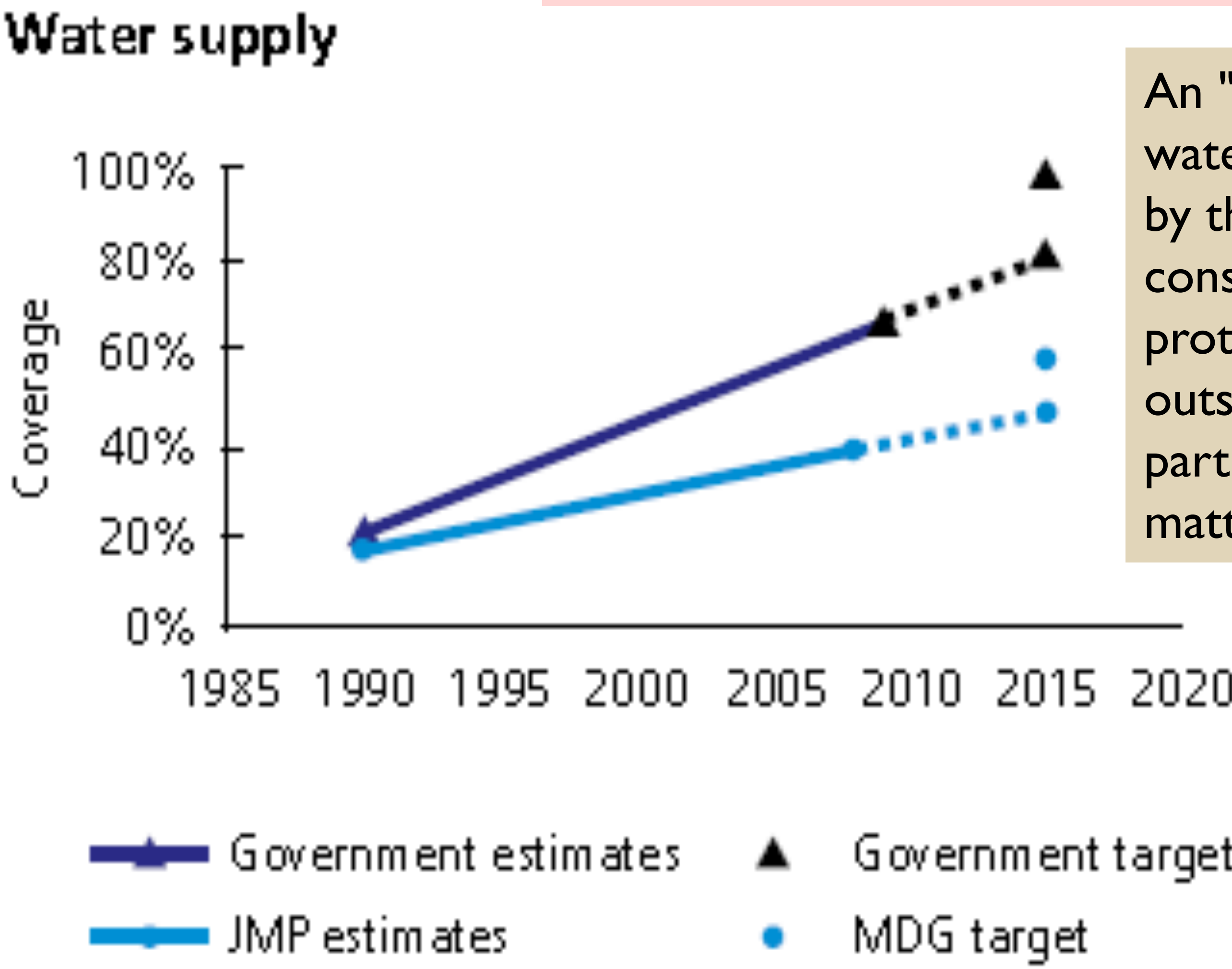
Fluoride Content of Local Tea Infusions

N o.	Tea brands	Number of brands tested	Mean fluoride content (mg/kg)
1	Green tea bags	2	245-265
2	Black tea leaves	10	302-728
3	Black tea bags	3	258-300

Samuel Zerabruk, Bhagwan Singh Chandravanshi and Feleke Zewge (Bull. Chem. Soc. Ethiop. 2010, 24(3))

Water Supply Coverage: Ethiopia(Cont'd)

Source: JMP 2010 report



An "improved drinking-water source" is one that by the nature of its construction adequately protects the source from outside contamination, in particular from faecal matter.