Center *of* Advanced Materials *for* the Purification of Water *with* Systems

Nanotechnology for Sustainable Water Supply: Nexus to Economic Output, Energy, Health, and Environment

Mark A. Shannon
Director *WaterCAMPWS*
Micro-Nano-Mechanical Systems Laboratory
Mechanical Science and Engineering
University of Illinois

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What is the *WaterCAMPWS?*

- Center of Advanced Materials for the Purification of Water with Systems
- Science and Technology Center Awarded late 2002, $4 m/yr from NSF, $400k Illinois, $600k from companies and other sources
- 10 universities, 7 partners, 14 industrial affiliates, ~120 students, ~50 faculty

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Mission and Purpose of the *WaterCAMPWS*

Our mission is to develop **revolutionary new materials and systems** to purify water for *human use*.

Our purpose is to educate a diverse body of students and the public in the *value, science, and technology* of water purification.

My purpose today is to talk about the problems to sustainably supply water for human needs, and how nanotechnology can dramatically improve these problems, and lead economic growth.

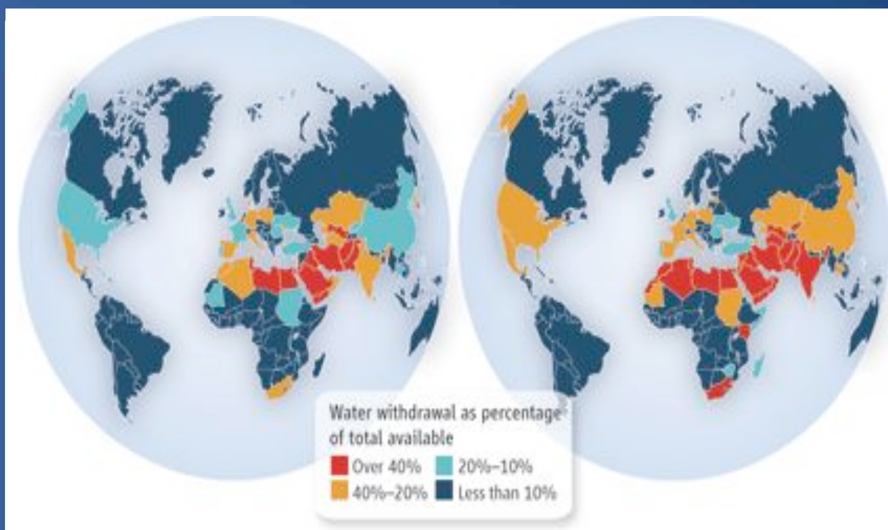
Value of Water

- Low Cost: Cheapest, highest quality product produced
- Impact Huge: Energy, agriculture, livestock, industry, homes, health
- Affects EVERY Aspect of Economy: More water, higher quality, lower cost, more wealth
- Traditional Concerns: Safety and health

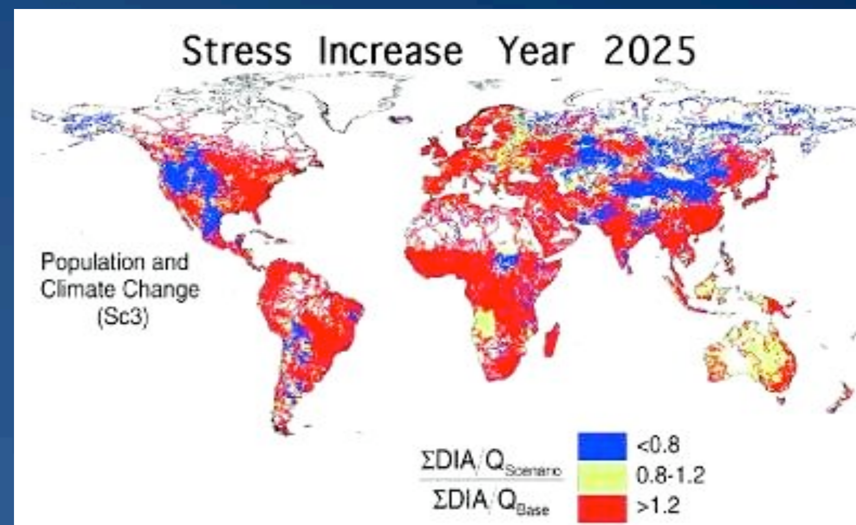
**HARD TO OVERESTIMATE IMPORTANCE,
BUT TAKEN FOR GRANTED BY MANY IN THE INDUSTRIAL WORLD: THIS WILL CHANGE, EVERYONE EVERYWHERE WILL BE AFFECTED IF WE FAIL TO PROVIDE CLEAN WATER.**

Major Problems Facing World

- 1.2 Billion people at risk from lack of clean water
- 2.6 Billion people lack adequate sanitation
- It is only going to get worse



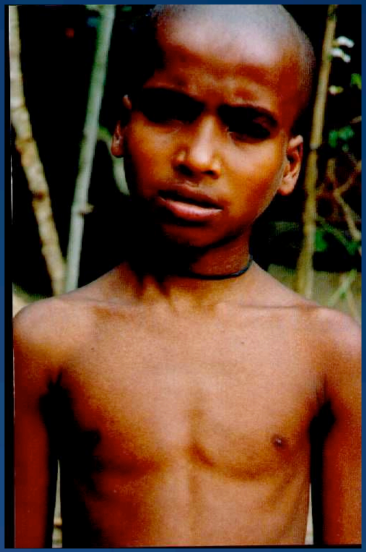
World Map showing water consumption world-wide as percentage of total available water.



World Map showing affect of population and climate change on water stress.

Major Problems Facing World

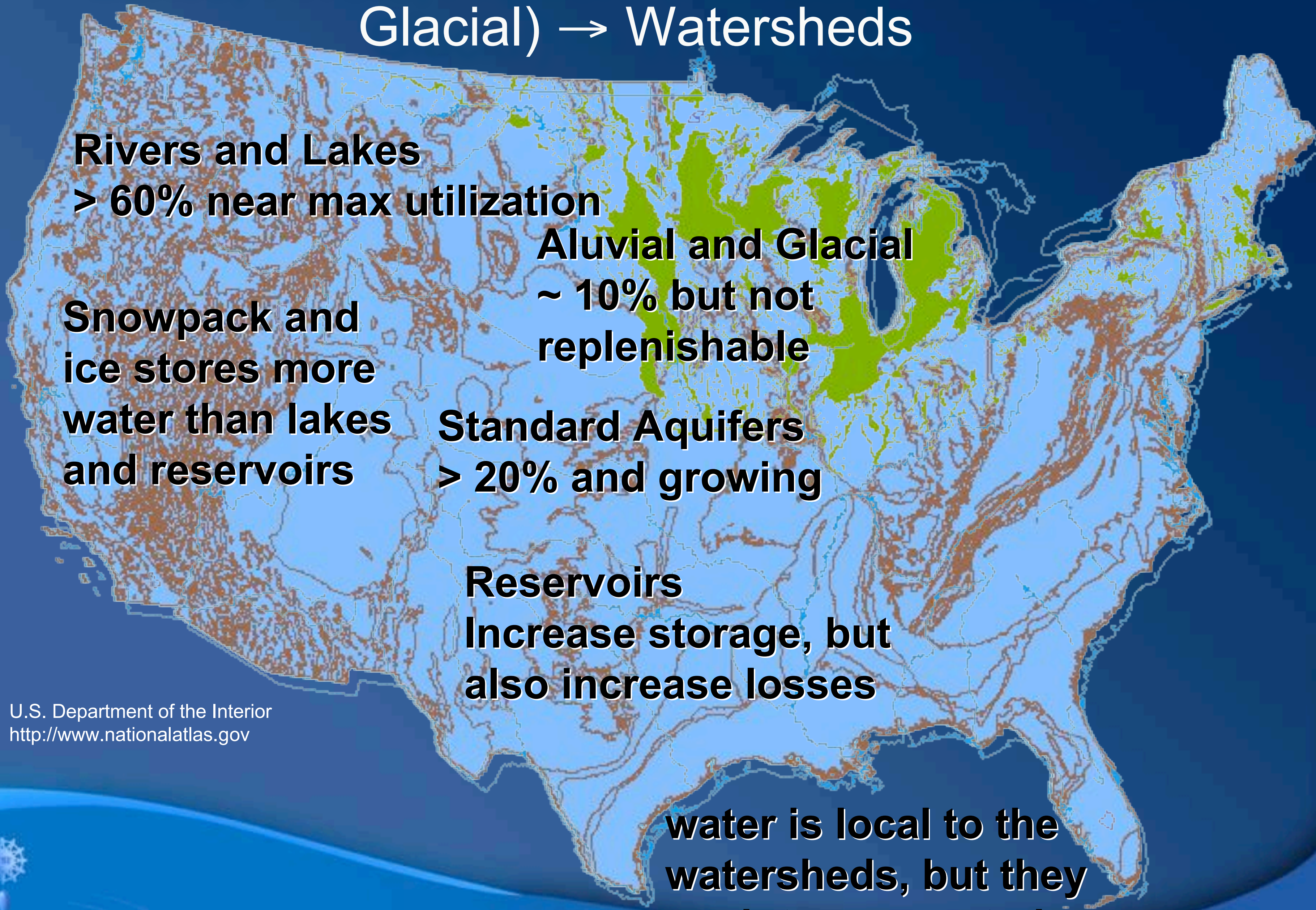
- 35% of people in developing world die from water related problems, over 2 million/year
- Diarrheal diseases from bad water a leading cause of malnutrition and food pressures
- 27 children die every 10 minutes from water problems
- 30 plus million in Bengal suffer from arsenic poisoning



Mega-Trends Making it Worse

- Era of Infrastructure Replacement: $550/capita owed in U.S.
- Population Growth: >1% per year drives increase demand in water, food, and energy: Overpumping of aquifers
- Energy Growth: Largest withdrawal of water for mining, refining, and generation of electricity
- Contamination of Source Waters: Increasing and cross-contamination of surface and aquifers is growing, reducing dilution solutions – *more aggressive treatment and new facilities needed.*
- Snowpack storage and glacial melting: Major river systems will see periodic shortages during dry months (Brahmaputra, Ganges, Yellow, Yangtze, and Mekong Rivers that serve China, India, and Southeast Asia, Western U.S., Africa)

Lakes, Rivers, Aquifers (Standard, Aluvial, and Glacial) → Watersheds



Rivers and Lakes
> 60% near max utilization

Snowpack and ice stores more water than lakes and reservoirs

Aluvial and Glacial
~ 10% but not replenishable

Standard Aquifers
> 20% and growing

Reservoirs
Increase storage, but also increase losses

water is local to the watersheds, but they are interconnected

U.S. Department of the Interior
http://www.nationalatlas.gov

Aquifers - Currently Stressed (Red) and Impacted (Yellow) by Over-Pumping in U.S. Alone

Significant loss to "fossil" aquifers, in U.S., China, India, and throughout the world

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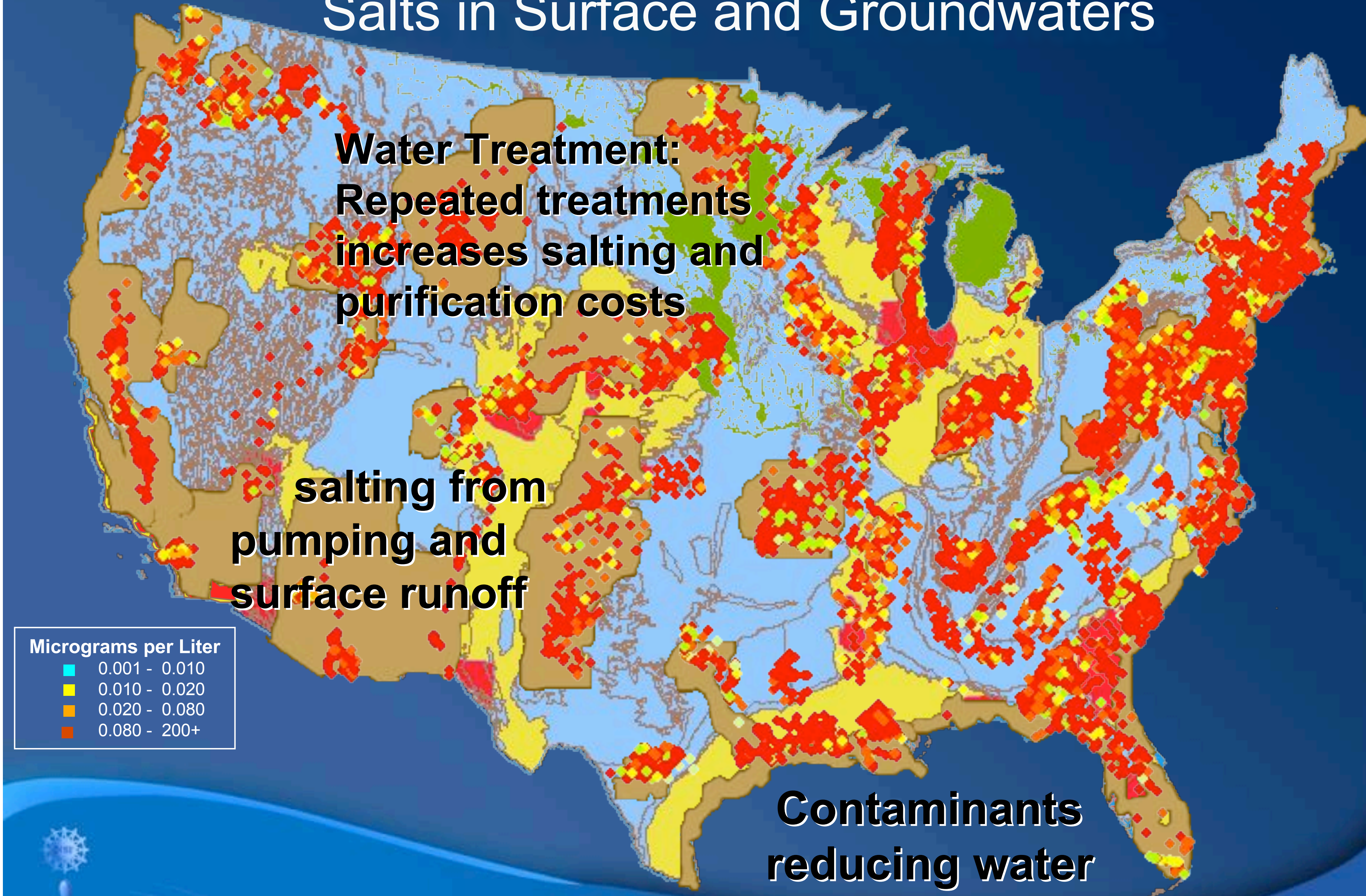
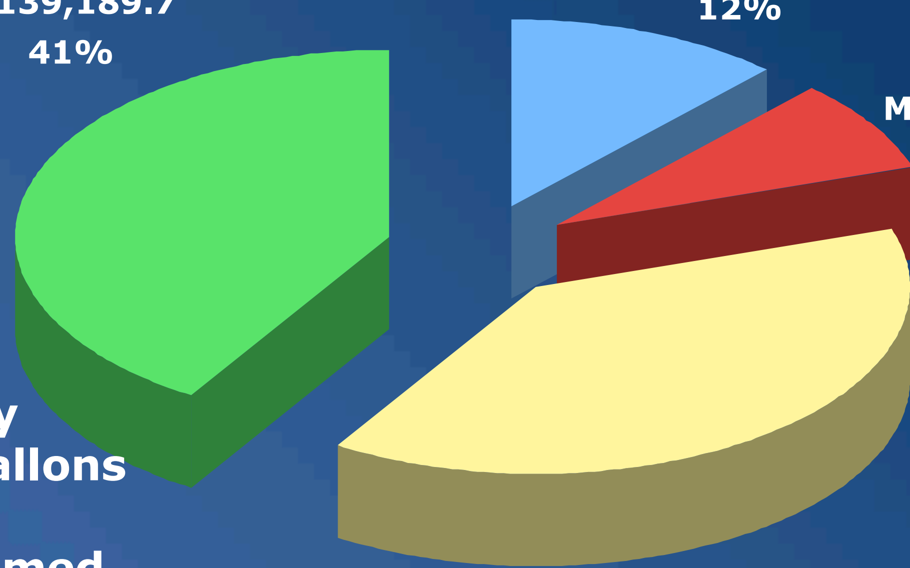
EPA Critical Drinking Water Contaminants and Salts in Surface and Groundwaters



Volume of Water Withdrawn for All Uses

(Million Gallons per Day)



Total Water Withdrawn per day
339,487 million Gallons

Total Water Consumed per Year
123.9 Trillion Gallons

costs directly related to withdrawals: source matters

"Consumptive Water Use for U.S. Power Production,
P. Torcellini, et.al., National Renewable Energy Laboratory, 2003.

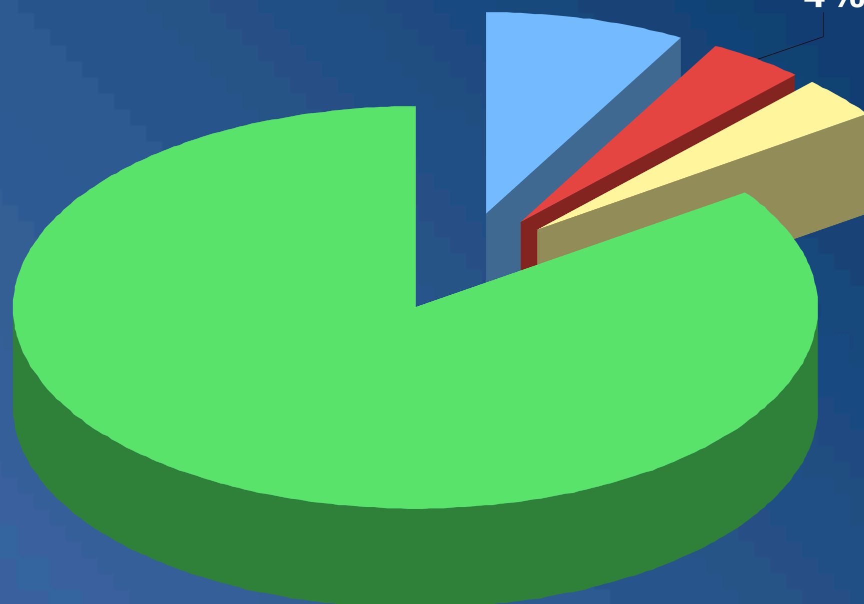
Volume of Water Consumed

Total Water Consumed per day 100,320 million Gallons

Total Water Consumed per Year 36.6 Trillion Gallons

~30% of withdrawn

(Million Gallons per Day)



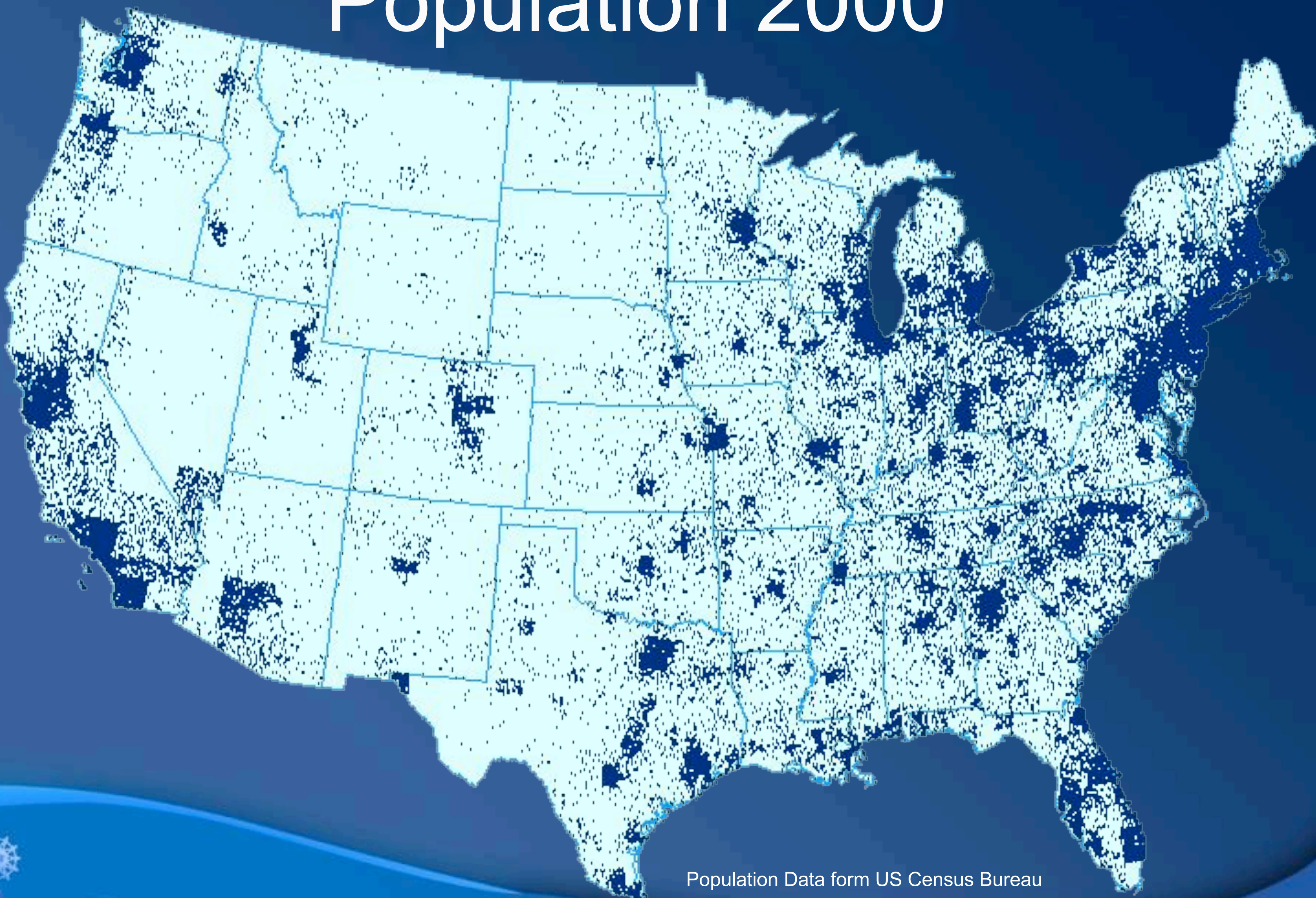
consumption directly affects source amounts available

"Consumptive Water Use for U.S. Power Production, P. Torcellini, *et.al.*, National Renewable Energy Laboratory, 2003.

Projections

- Population driven
- Application driven
- Source driven
- Energy driven

Population 2000



Population Data form US Census Bureau

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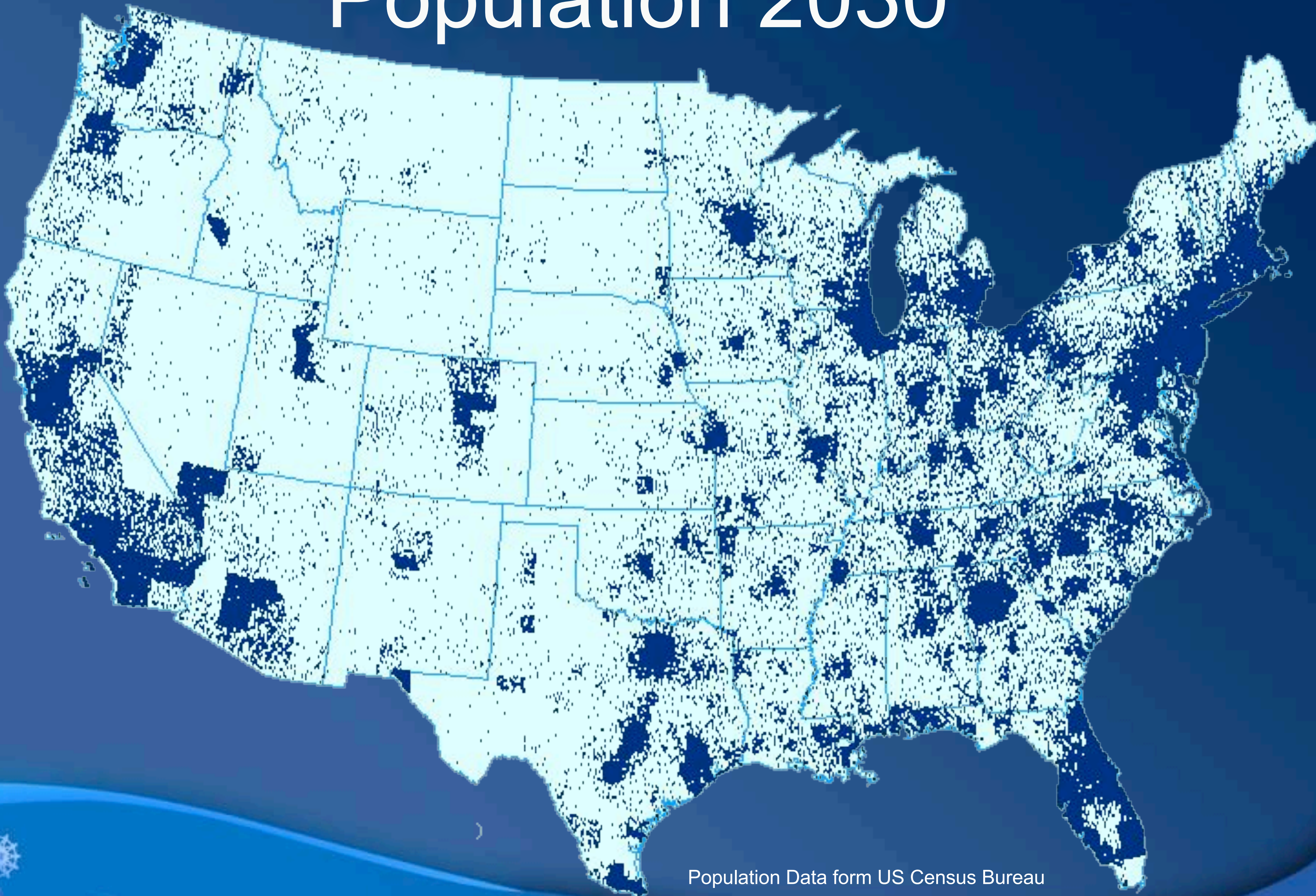
Population 2030



Population Data form US Census Bureau

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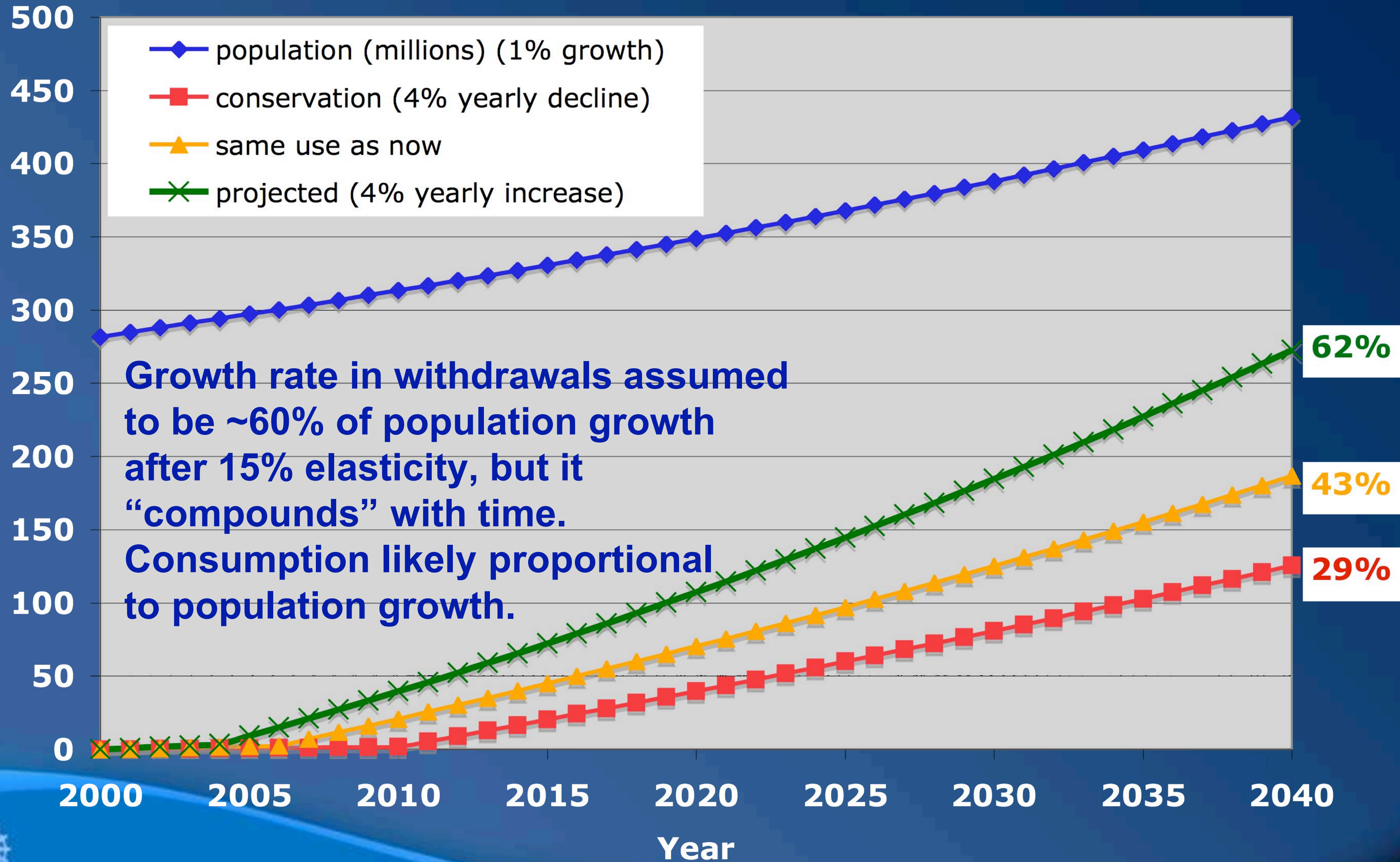
Water Use Growth With Population

Increase in Million Acre Feet (325,500 gal) of Water Withdrawn



Population Data form US Census Bureau

2030 Projected % Increase (since 2000)

Averages don't tell the real story:
Growth problems will be local.

Population data and projections from U.S. Census Bureau
http://www.census.gov/population/www/projections/stproj.html
http://www.census.gov/popest/datasets.html
Water Use Data from USGS (http://web1.er.usgs.gov/NAWQAMapTheme/index.jsp)
Projections for water use based on Texas Water Use 60 yr projections
(http://www.twdb.state.tx.us/publications/reports/State_Water_Plan/2007/2007StateWaterPlan/2007StateWaterPlan.htm)

Economic Issues with Potable Water

- More than $1 trillion (2001 dollars) spent on water treatment, in past 20 years
- More than $1 trillion (2001 dollars) more needed for infrastructure, and treatment in next 20 years
- Demand for potable water currently exceeds available resources in many parts of world. New water technology in next 35 years > $3 trillion
- One of the largest growth sectors in next two decades in the world
- Major water projects will require large capital at a time when it will potentially be scarce & expensive

Economic security at risk if lack of clean water

Energy and Water Nexus

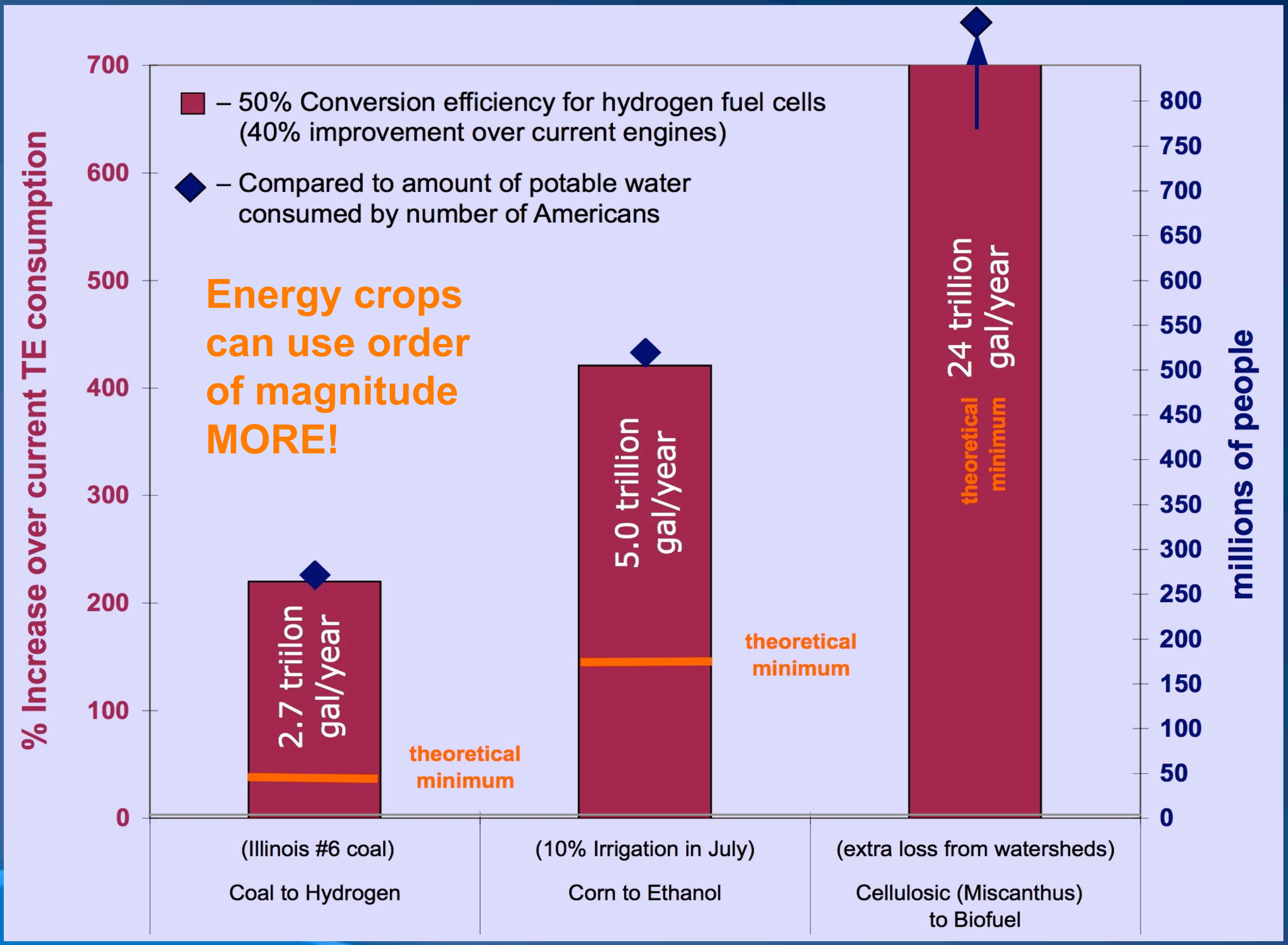
Without sufficient energy:

- We cannot supply sufficient clean water!

However, without sufficient water:

- Meeting the energy needs of the growing population will be impacted
- Transfer to a hydrogen economy, biomass and clean coal derived fuels will be impacted
- Oil shales and sands need huge amounts of water
- Plug-in hybrid vehicles will be impacted, from restricted electric generation

Trends in Water with New Energy



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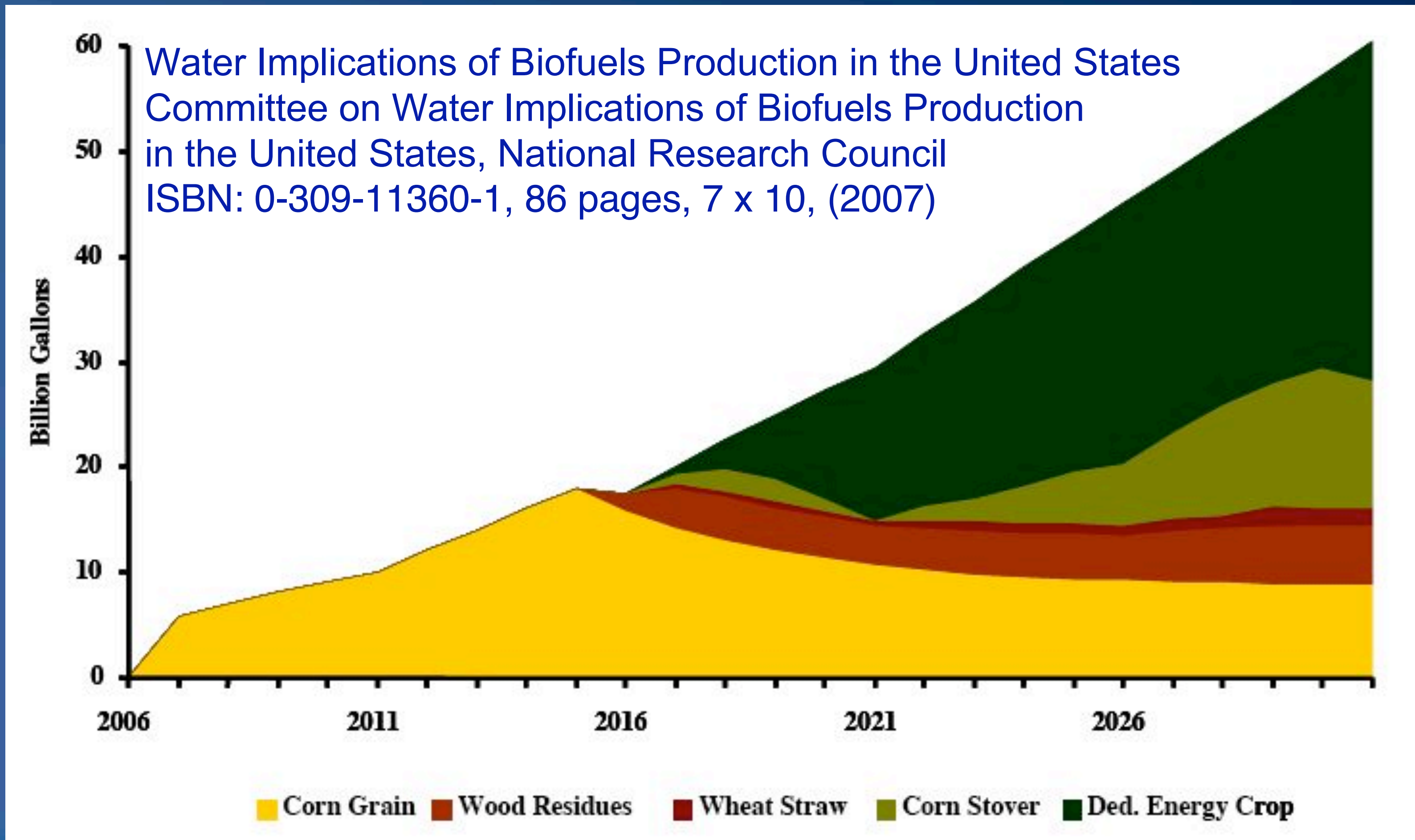
Trends in Biofuels

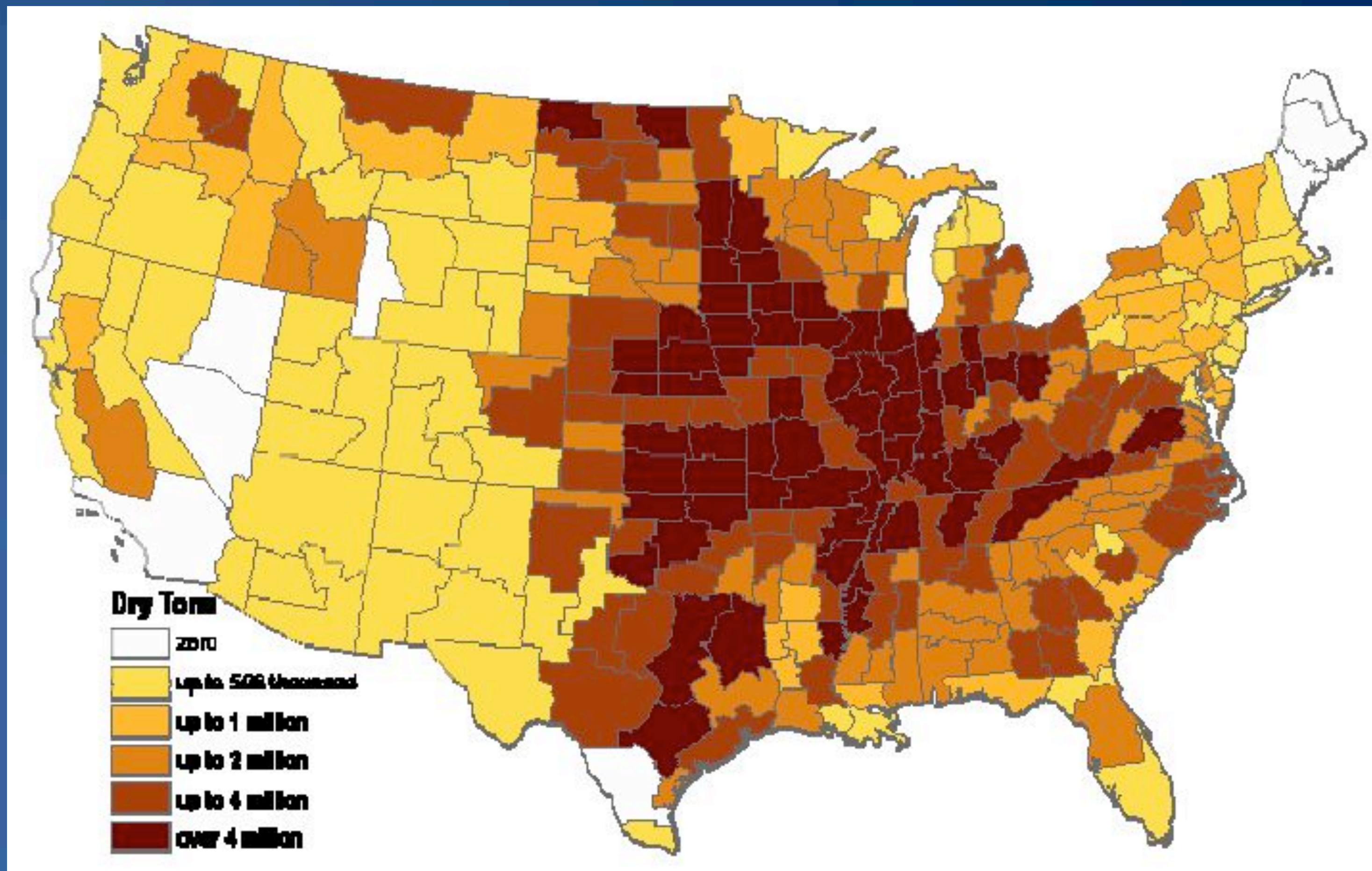
Projection of ethanol production by feedstock assuming cellulose-to-ethanol production begins in 2015.



SOURCE: Reprinted, with permission, from D. Ugarte, University of Tennessee, written commun., July 12, 2007.

Trends in Biofuels

Distribution of the production of cellulosic materials in dry tons by the year 2030.



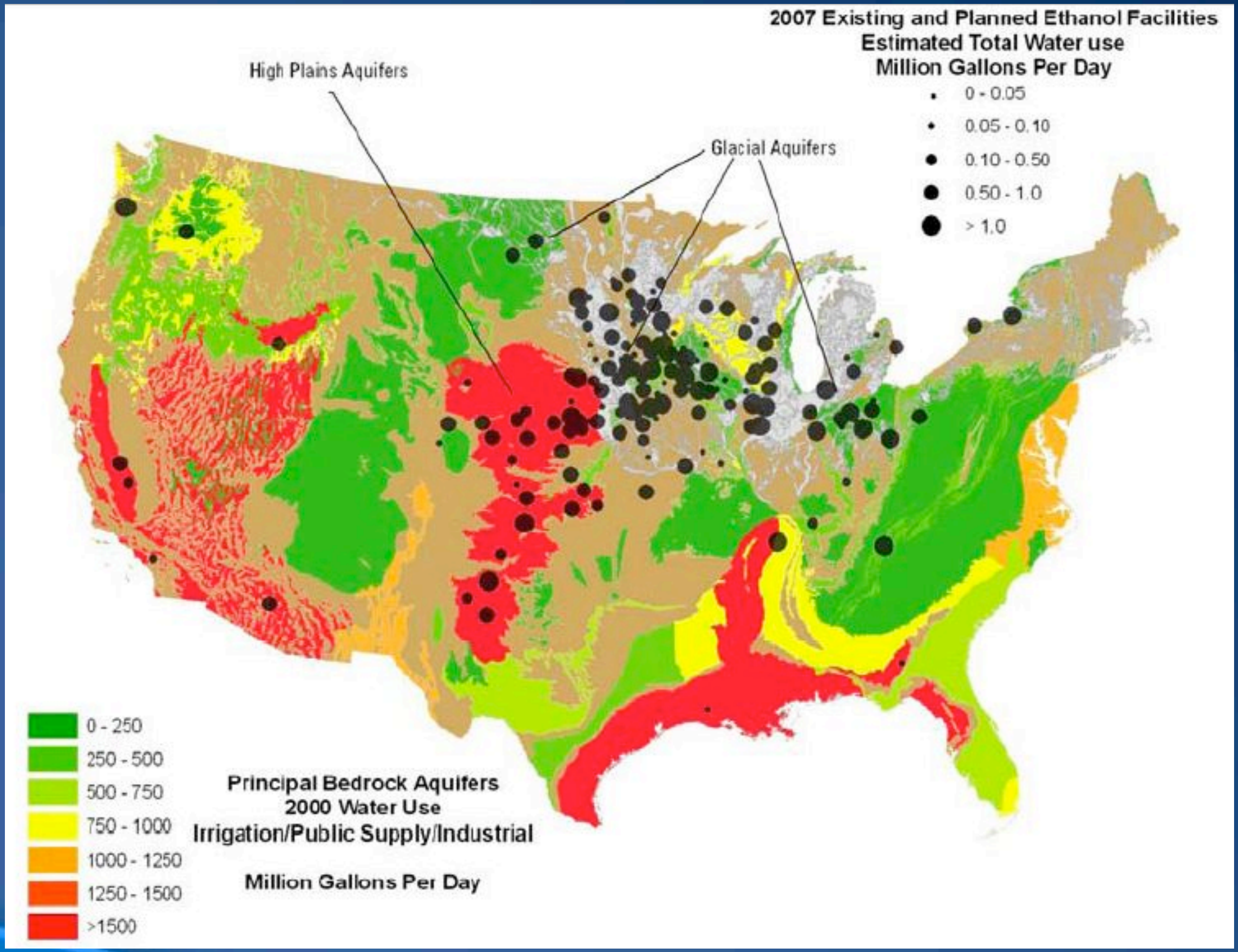
SOURCE: Reprinted, with permission, from D. Ugarte, University of Tennessee, written commun., July 12, 2007.

Impact of "New" Energy on Water

- Total water lost via evapotranspiration to generate sufficient energy from biomass: in excess of 140 trillion gallons per year.
  - Total Withdrawn U.S./yr currently ~ 124 T gal
  - Outflow Mississippi Basin/yr ~ 132 T gal
- Mean Rain Mississippi Basin ~ 835 mm/yr
- Need: Corn/soybean ~ 440 mm/yr. Energy Grasses ~ 550 mm/yr.
- Irrigated seed and field corn needed for ethanol add another 4 to 7 gal of water for each gal fuel
- Irrigating marginal land will need 1000 times more

Ethanol Refining Impact on Water

Existing and planned ethanol facilities (2007) and their estimated total water use mapped with the principal bedrock aquifers of the United States and total water use in year 2000.



SOURCE: Janice Ward, U.S. Geological Survey, personal commun., July 12, 2007.

Water for Ethanol Refining: Source Matters!

Industrial Processing Water Use in Minnesota, 2004

Category	Water Use, mgd Ground Water	Water Use, mgd Surface Water	Water Use, mgd Total
Agricultural processing (food & livestock)	25.2	0.1	25.3
Pulp and paper processing	2.3	80.3	82.6
Mine processing (not sand & gravel washing)	0.5	296.5	297.0
Sand and gravel washing	3.8	7.5	11.3
Industrial process cooling once-through	5.8	0.5	6.3
Petroleum-chemical processing, ethanol	10.9	0.4	11.3
Metal processing	3.9	0.0	3.9
Non-metallic processing (rubber, plastic, glass)	3.0	0.0	3.0
Industrial processing	1.0	0.0	1.0
Total	56.3	385.4	441.7

Source: MDNR Water Appropriations Permit Program, 2004

20% of aquifer draw

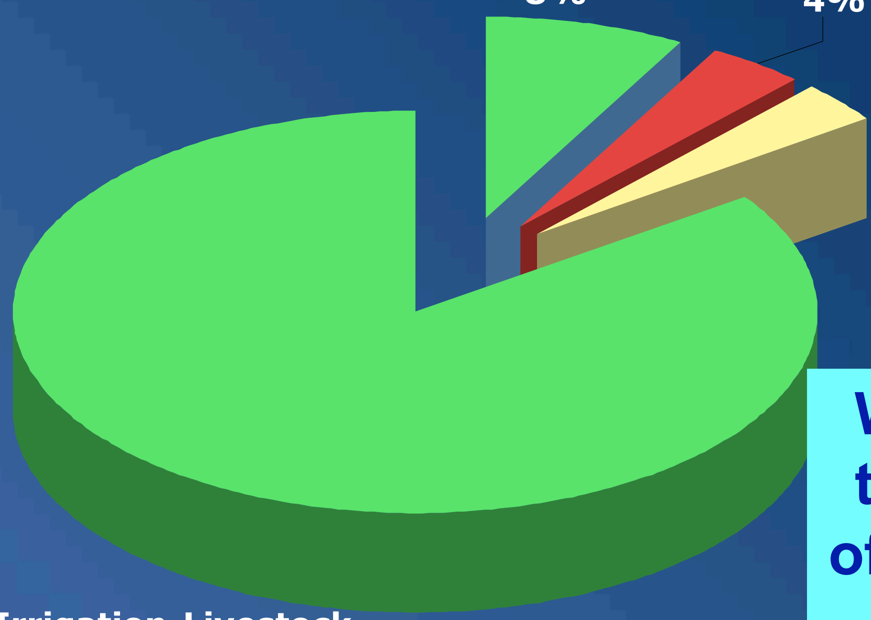
Volume of Water Consumed

(Million Gallons per Day)

If total amount consumed of the withdrawn water grows by just 6.5% to ~36.5% to account for new energy

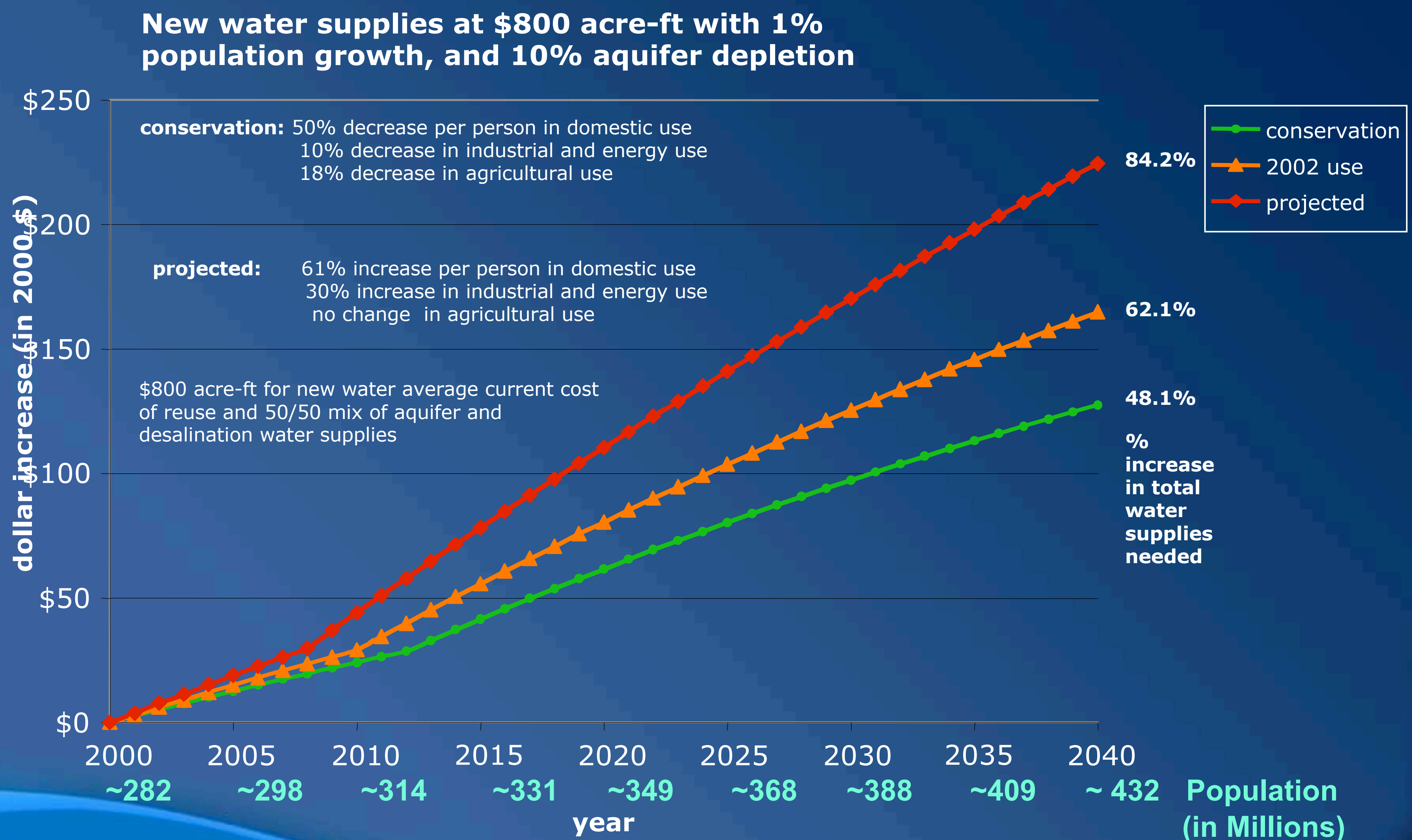
Total Water Consumed per Year
45.3 Trillion Gallons

INCREASE SAME AS ALL POTABLE WATER CONSUMED



What happens to the consumption of all other sectors if "new" energy grows the Irrigation slice?

Water Cost Growth With Population



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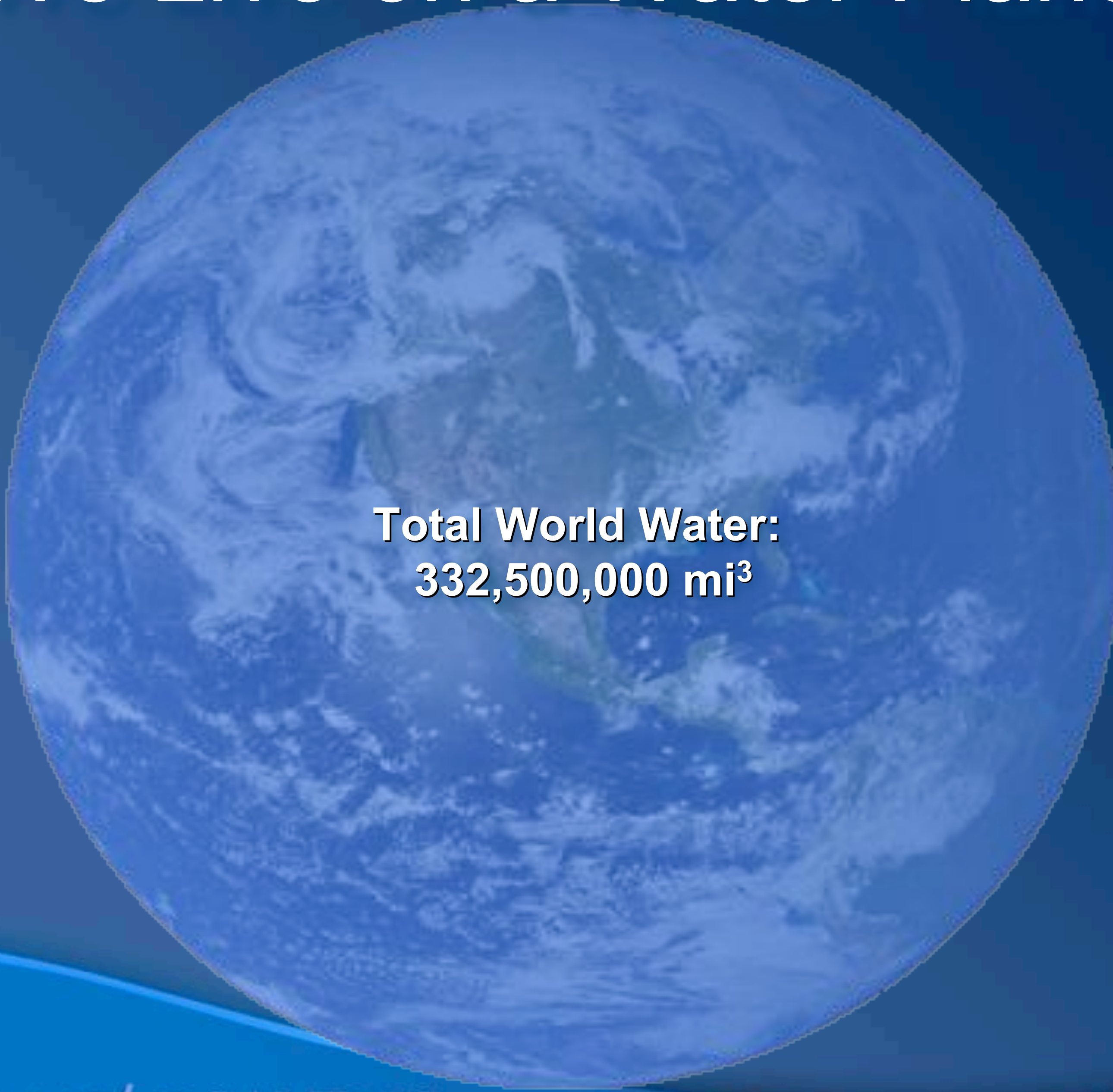
Water Problems Coupled & Growing

- Contaminated and impaired waters need research on how to sense and mitigate: Decontamination
- Population, energy and agriculture growth need research in how to increase water supplies: Desalinate and Reuse
- Health and viral threat, as well as global disaster in waterborne illness need research to make water safe from pathogens: Disinfection
- **Population growth exacerbates problems**: Impacts energy, food, health, water withdrawals, contaminated sources, more aquifer depletion, …

But there are good reasons for hope!

We Live on a Water Planet



Total World Water:
332,500,000 mi^3

Where is our Water?

Ice Caps, Glaciers, & Perm. Snow
1.74%
5,773,000 mi^3
(68.7% fresh)

Ground Ice & Permafrost
.022%
71,970 mi^3
(.86% Fresh)

Saline Lakes
.006%
20,490 mi^3

Saline Groundwater
.94%
3,088,000 mi^3

Accessible With Additional Research

Currently Accessible for Human Use

30% shortfall in 30 yrs

Lakes
.007%
21,830 mi^3
(.26% fresh)

Rivers
.0002%
509 mi^3
(.006 Fresh)

Groundwater
.76%
2,526,000 mi^3
(30.1% fresh)

Atmosphere
.001%
3,095 mi^3
(.04% Fresh)

Biological
.0001%
269 mi^3
(.0036% Fresh)

Swamps
.0008%
2752 mi^3
(.03% fresh)

Soil Moisture
.001%
3,959 mi^3
(.05% Fresh)

99.23% currently unusable for most humans

Why Aren't Saline Waters Used More?

- Current methods energy intensive
- Current methods capital intensive
- Current methods are chemically intensive
- Current methods are operationally intensive
- Current methods are prone to fouling, scaling, and/or corrosion
- Inland salt waters are full of hard salts, and disposal of brine is very expensive.

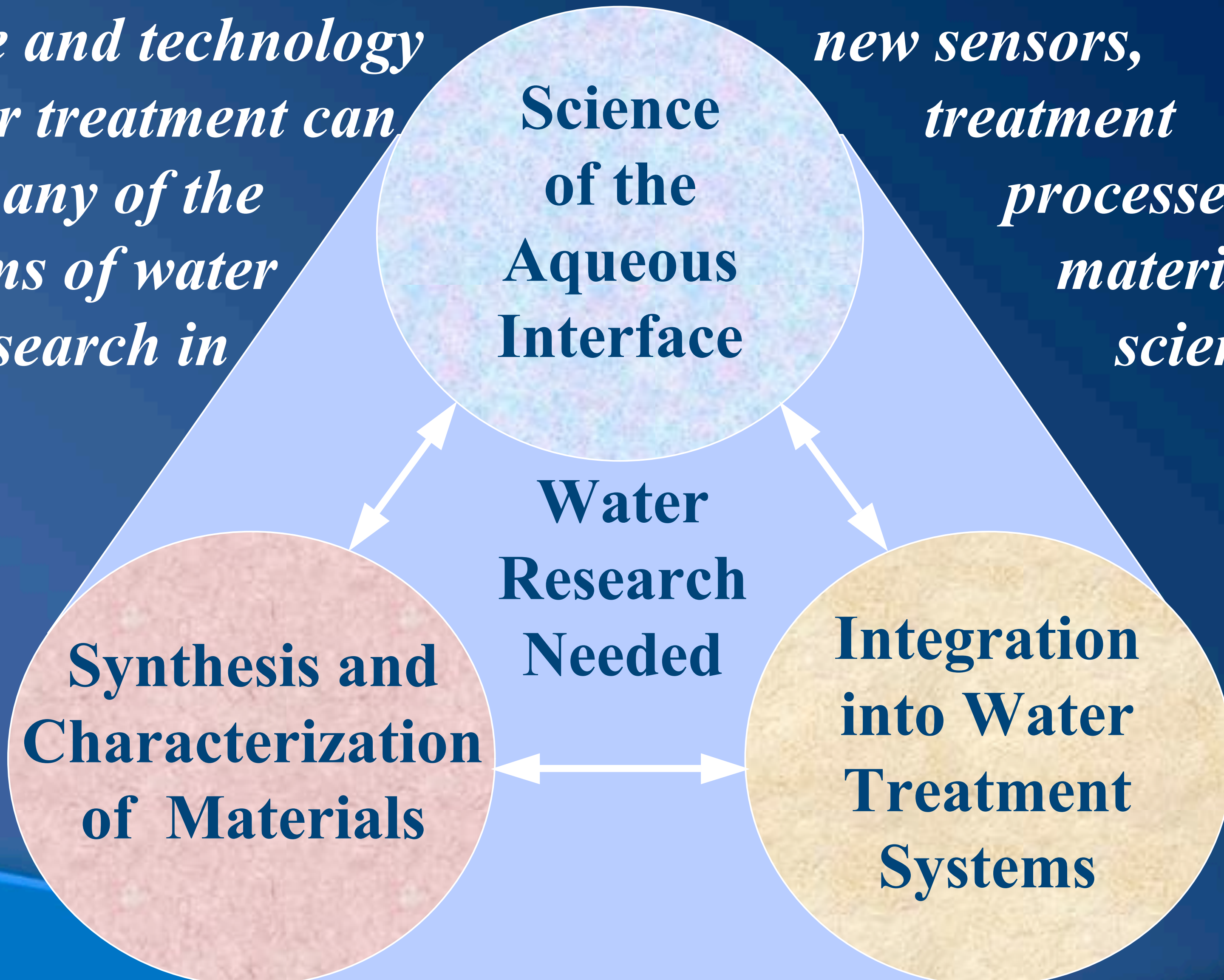
Even if energy free, desalination still $$

Many Opportunities

- Physically, we are far from the thermodynamic limits for separating unwanted species from water.
- Traditional methods chemically intensive, expensive, and not suitable for most of the world.
- New materials are being developed that exploit physics of the nanoscale at the water interface.
- New systems based on nanotechnology can dramatically alter the energy/water nexus.
- Huge gains in efficiency and productivity in water can drive economic growth, since current practice is wasteful, generating new capital and standard of living increases, similar to information-driven growth.

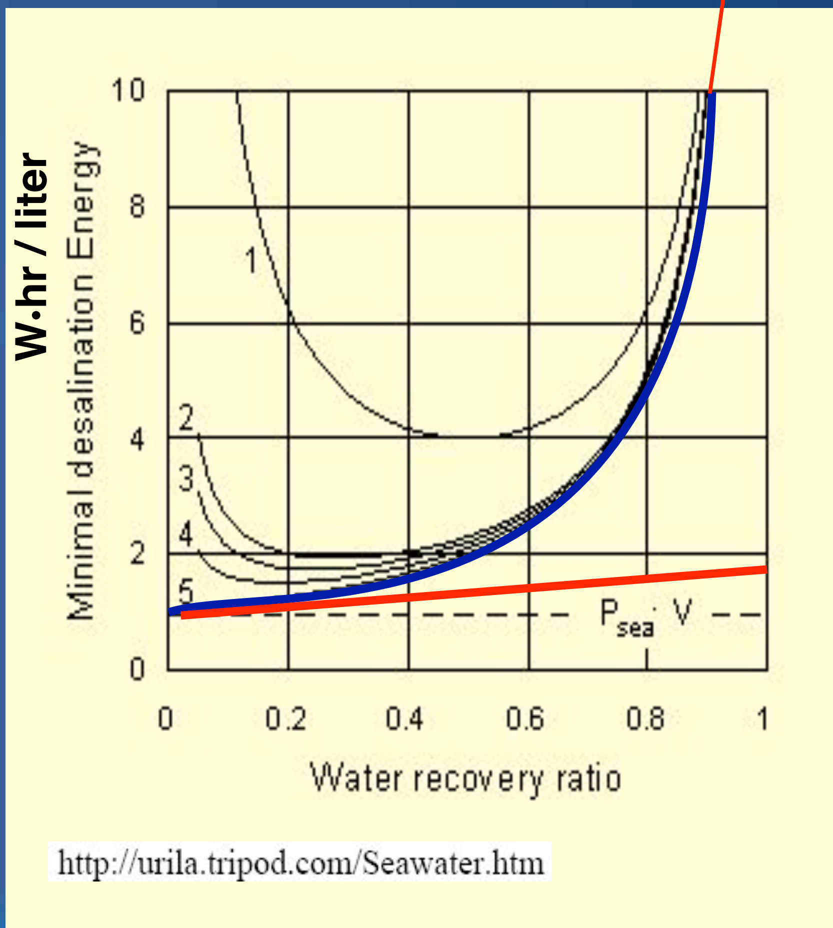
Science, Synthesis and Systems

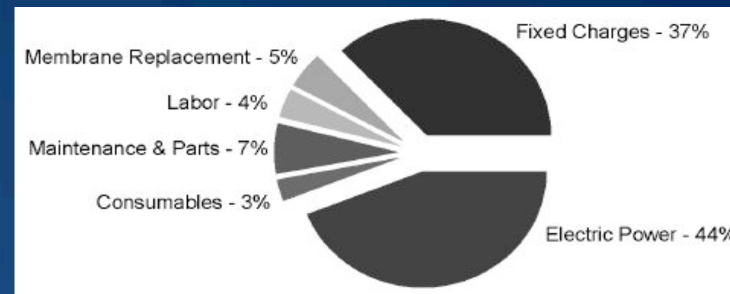
Science and technology of water treatment can solve many of the problems of water with research in new sensors, treatment processes & material science.



Reverse Osmosis: State-of-the-art

Least amount of energy possible



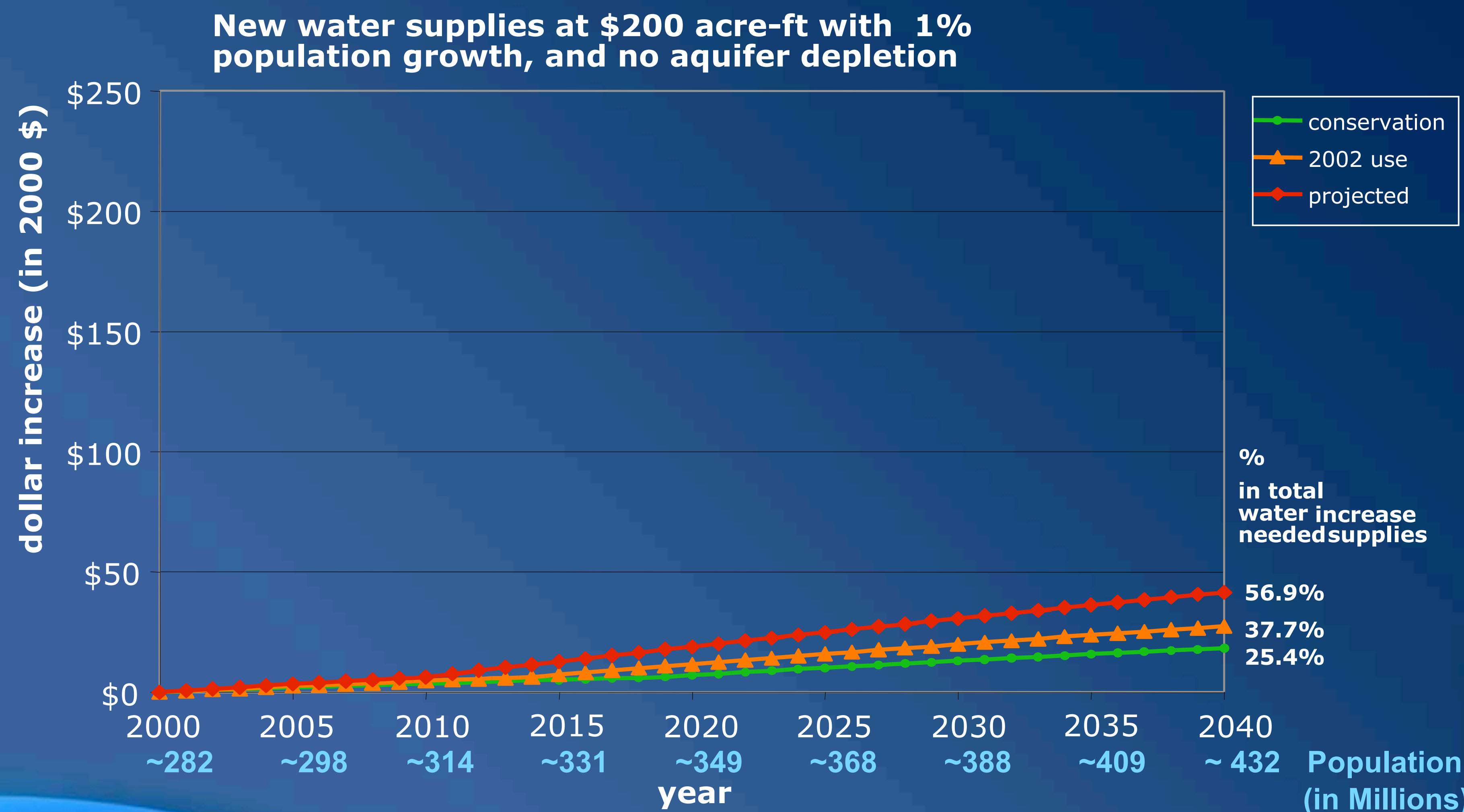


For water with 34,000 ppm TDS:

- 50% water recovery
  min Elec. 1.77 W·hr/liter
  best Elec. 2.22 W•hr/liter
- 80% water recovery
  min Elec. 5 W·hr/liter
  best Elec. 8.40 W•hr/liter

But Physical Limit is only 0.8 W•hr/liter for full recovery (no residual)

Water Cost Growth With Research



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How Do We INCREASE the Amount of Clean Water Available to People?

Three major goals:

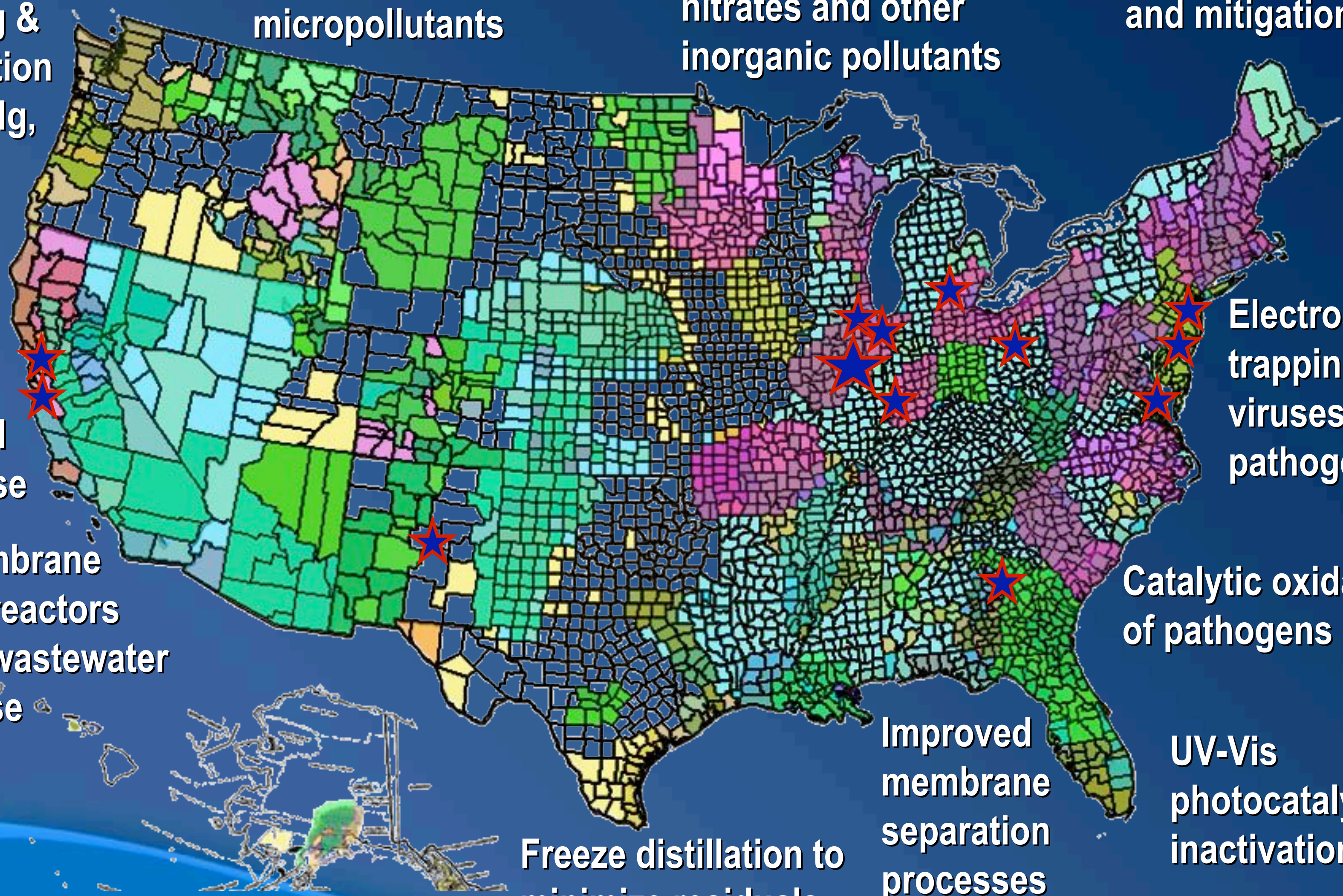
Goal I. Increase drinking water supplies, to gain new waters from **reuse** and **desalination** from the *"sea to sink to the sea again."*

Goal II. Selectively remove contaminants from all types of water sources, to get the *"drop of poison out of an ocean of water."*

Goal III. Disinfect water from current and potentially emerging pathogens **without producing toxic substances**, to *"beat chlorination."*

Nanotechnology plays a role in all.

Research Being Worked On By *WaterCAMPWS*



Selective sensing & adsorption of Pb, Hg, etc.

Catalytic oxidation of micropollutants

Catalytic reduction of nitrates and other inorganic pollutants

Fouling studies and mitigation

SFVS & new probes of material response

Electrostatic trapping of viruses and pathogens

Membrane Bioreactors for wastewater reuse

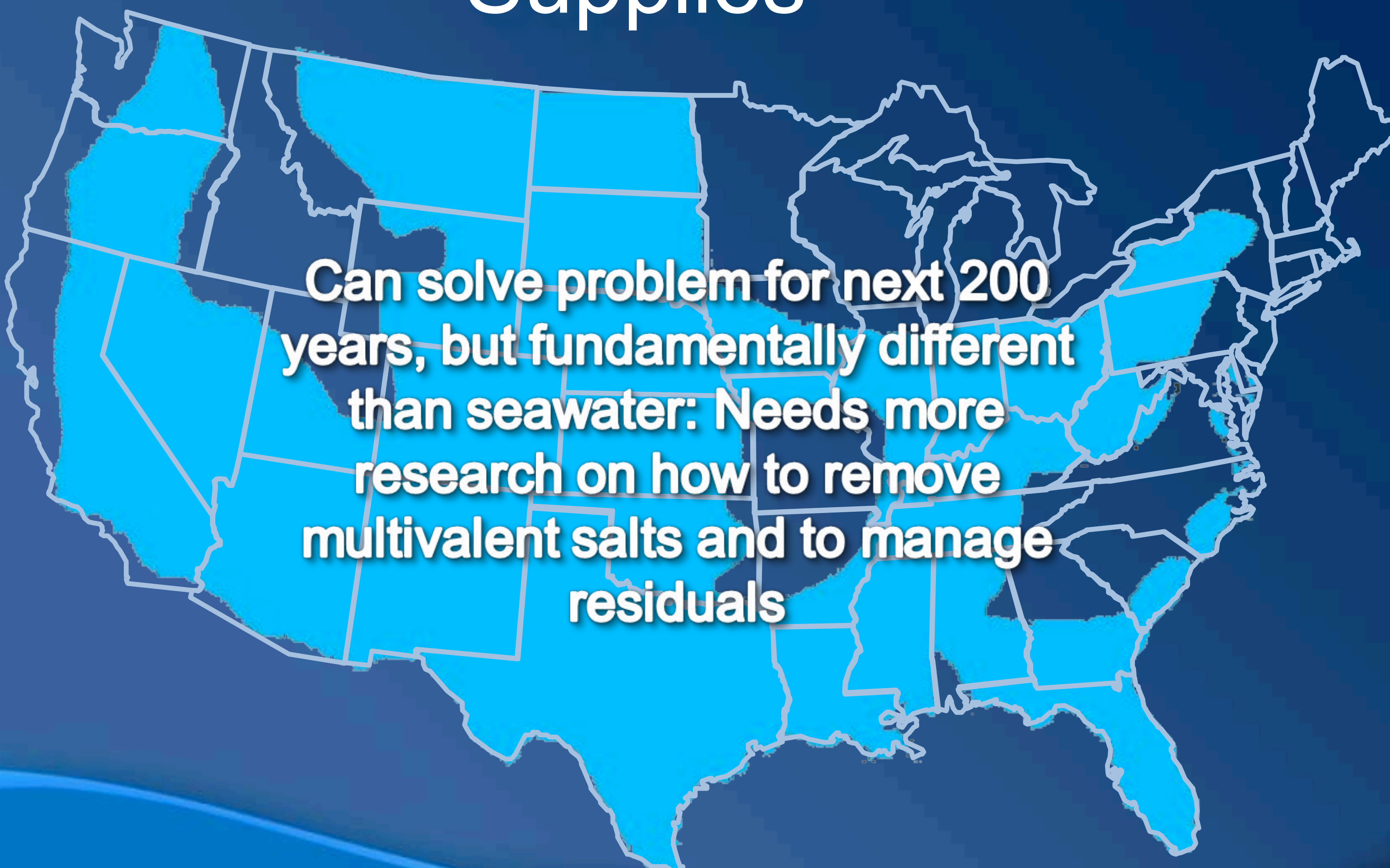
Catalytic oxidation of pathogens

Freeze distillation to minimize residuals

Improved membrane separation processes

UV-Vis photocatalytic inactivation

Inland Saline and Seawater Supplies

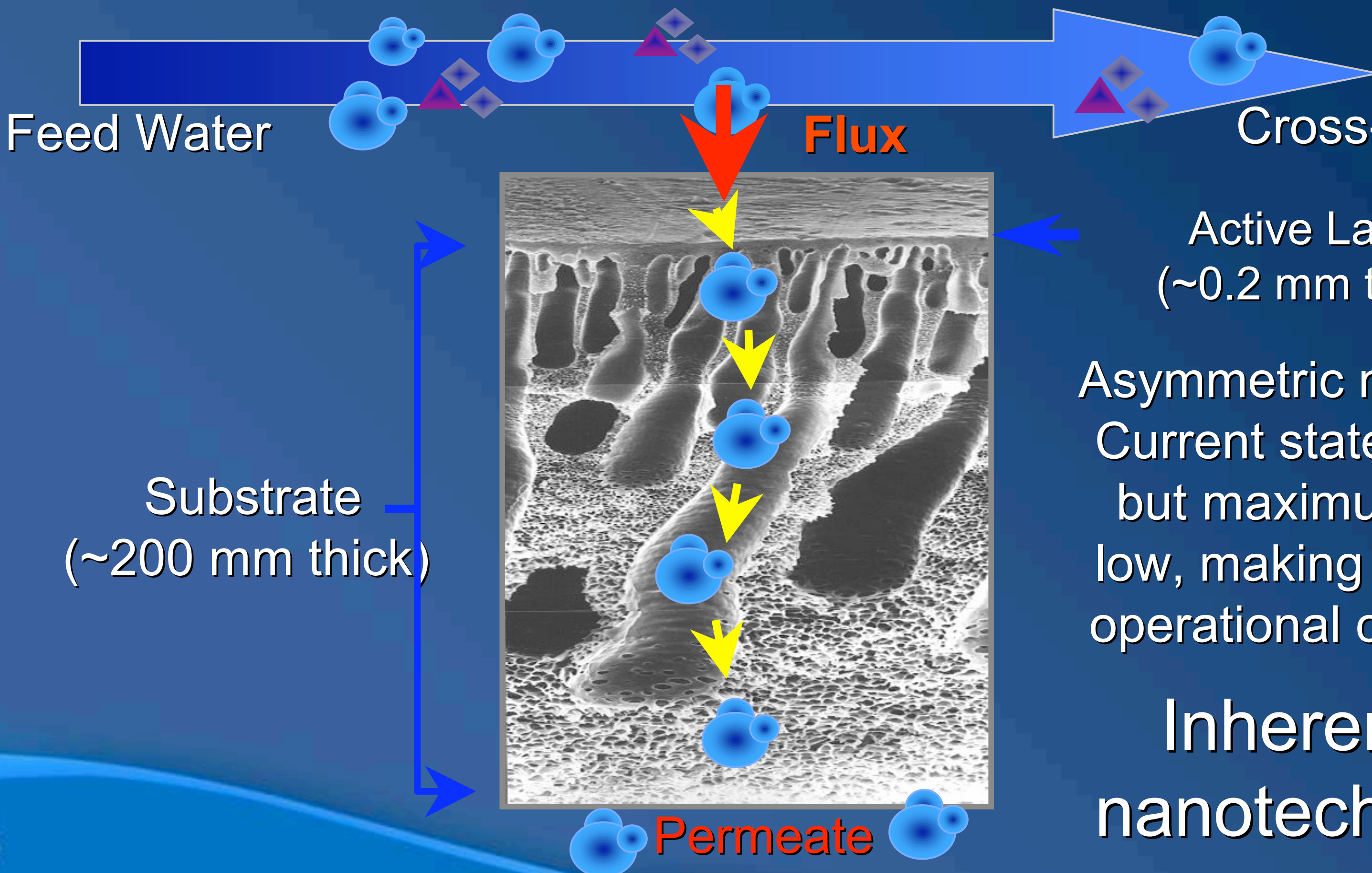


Can solve problem for next 200 years, but fundamentally different than seawater: Needs more research on how to remove multivalent salts and to manage residuals

Desalination & Water Purification Technology Roadmap SNL& BoR (2003)

Desalination by Reverse Osmosis

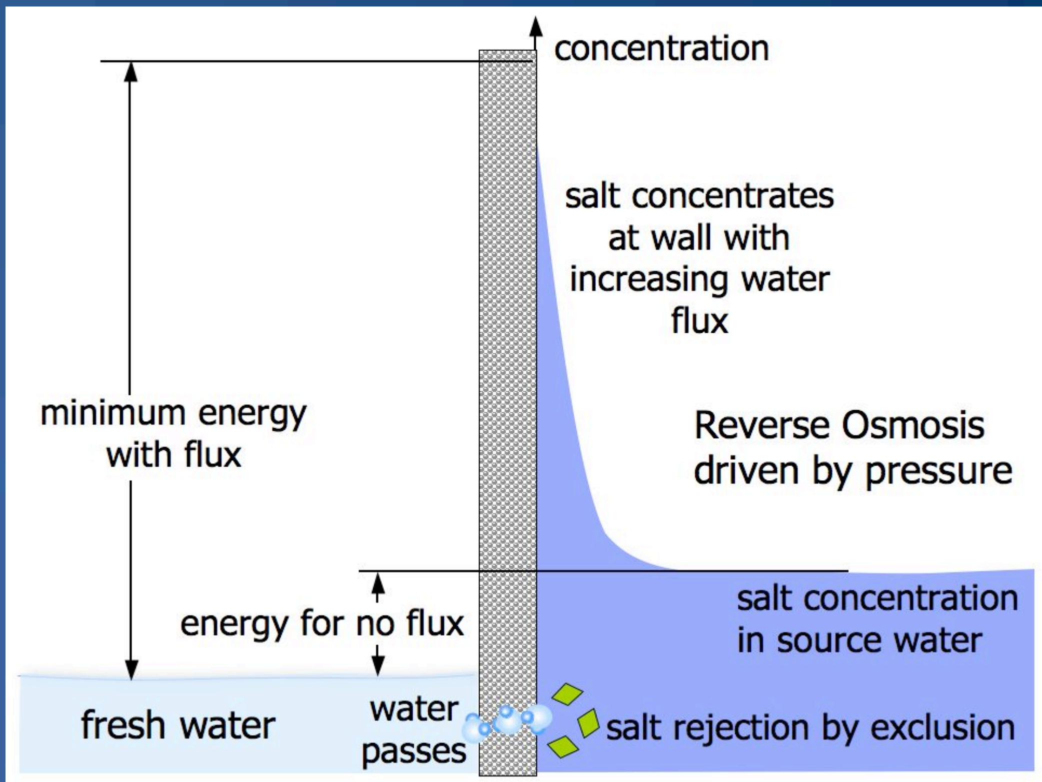
RO has been around a long time, worked reasonably well, but much more can be done.



Asymmetric membranes: Current state of RO art, but maximum flux still low, making capital and operational costs higher

Inherently a nanotechnology

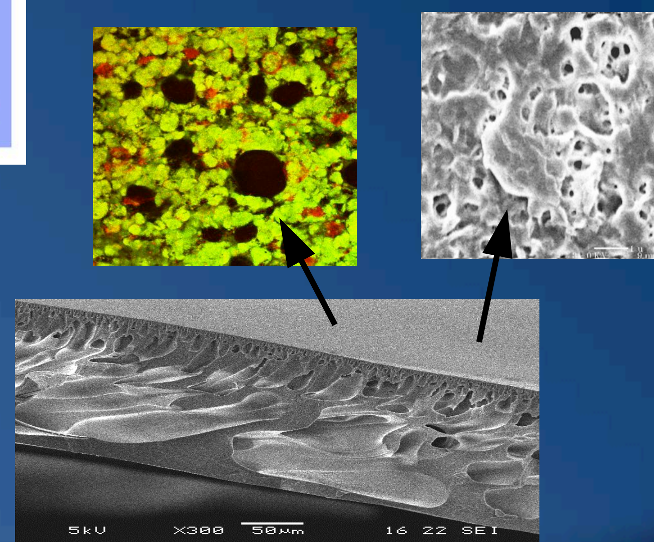
Problems with Reverse Osmosis



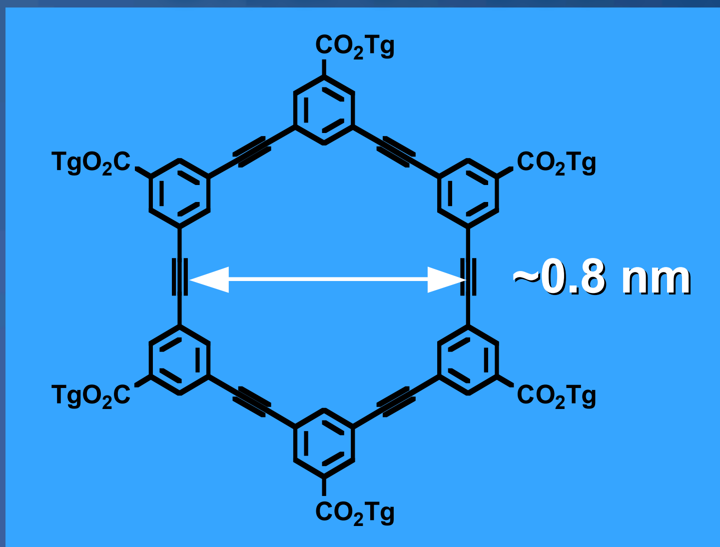
Low maximum flux, polarization also limits flux, and membranes foul!

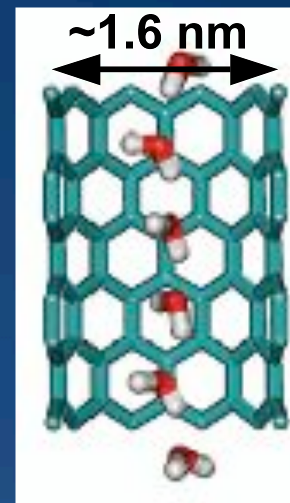
Low-Flux due to Size Exclusion and increasing Polarization Impedance with increasing flux

Surfaces and pores plug

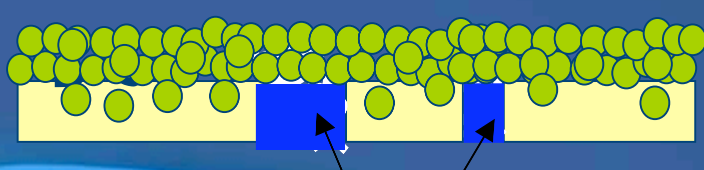


Increase Flux with Ultra-thin (<1 nm) Functionalized Rigid Star Amphiphiles and Ultra-smooth 1.6 nm Carbon Nanotubes





RSA active layer



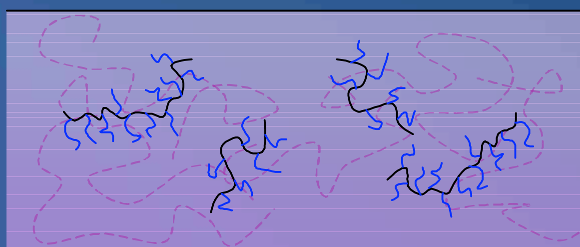
Moore and Mariñas 2007

<u>Comparison to commercial NF membranes</u>

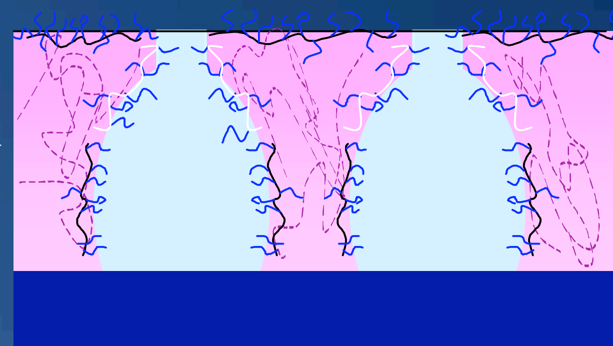
- RSA membranes (RSAMs) had 2x higher water permeability and comparable rejection.
- LLNL CNT membranes have an **order of magnitude higher flux** do to its hydrophobicity and atomic smoothness

Create Nano-Segregated Compounds within Membrane that Resist Fouling

graft copolymer added to casting solution



segregate and self-organize at membrane surfaces

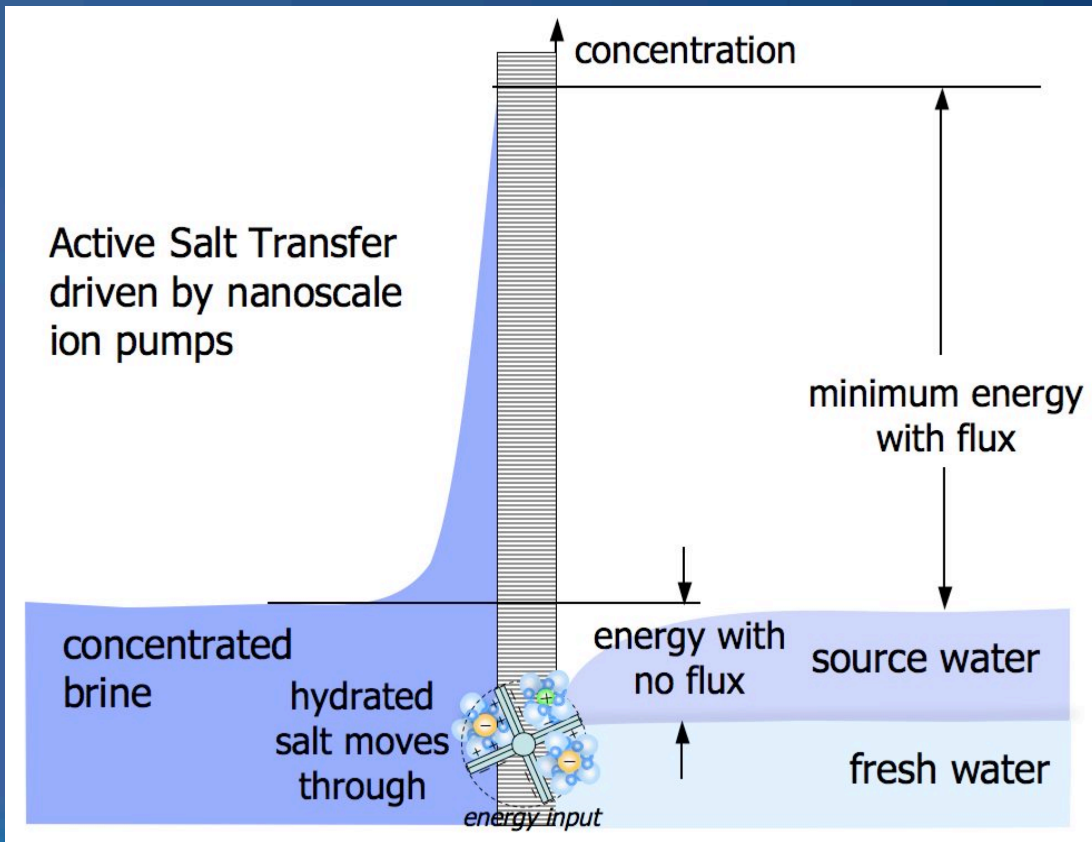


PEO brush layer on surface and inside pores

Fouling Resistance

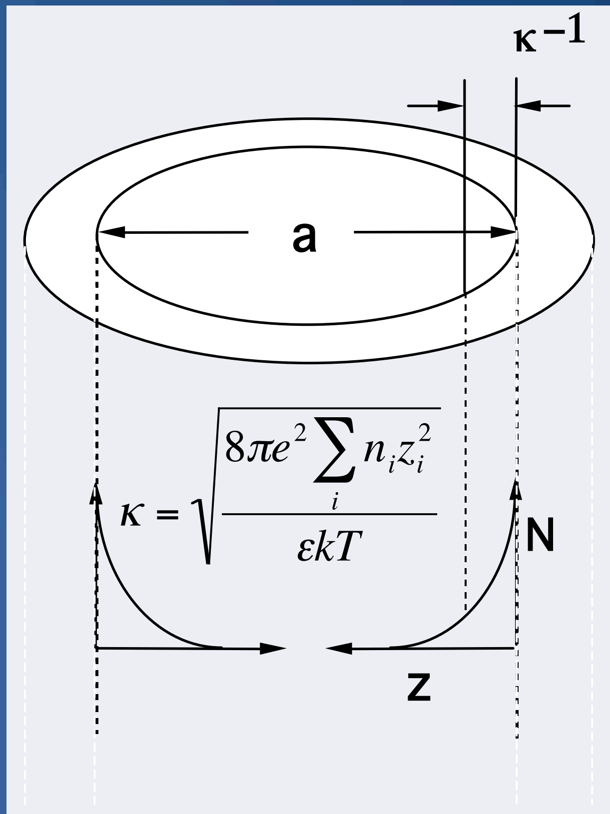
Asatekin, A., S. Kang, M. Elimelech, and A.M. Mayes, *Jour. Membrane. Sci.*, in press..

But Even a "Perfect" Membrane Still Slowed by Polarization Impedance

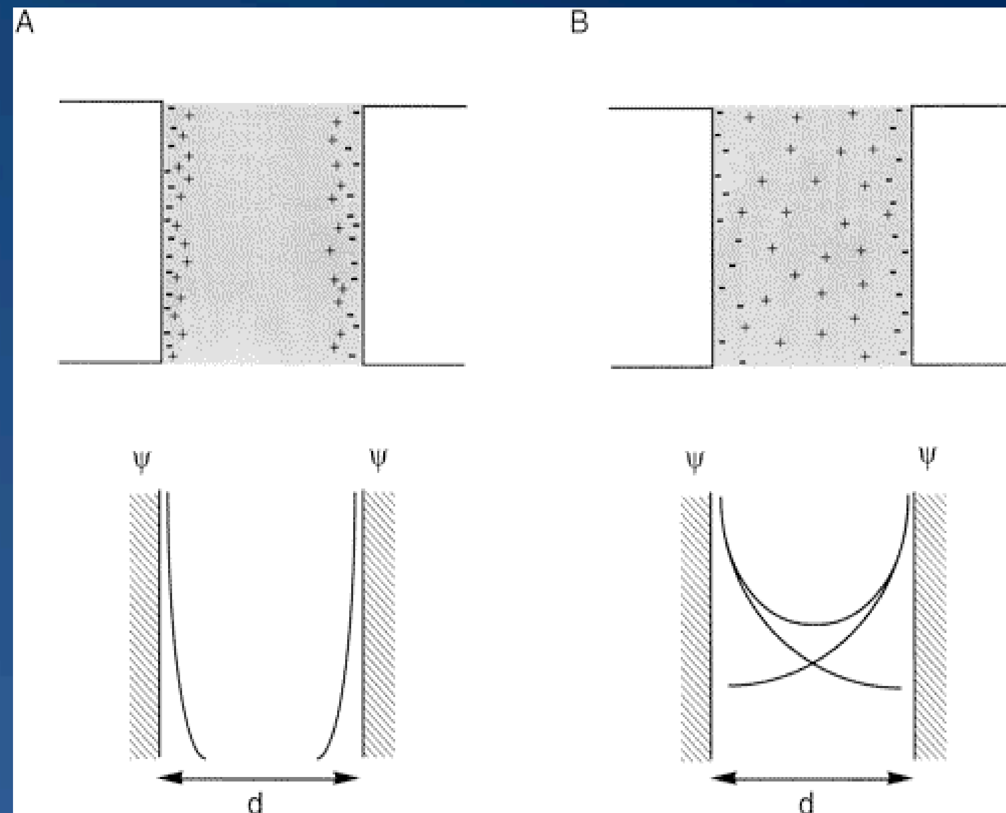


Active nano-channel ion pumps being developed to solve polarization impedance problem, BUT MUST BE NANOFLUIDIC FLOW!

When Will Nanofluidics Start to Dominate?



$$\kappa = \sqrt{\frac{8\pi e^2 \sum_i n_i z_i^2}{\varepsilon k T}}$$

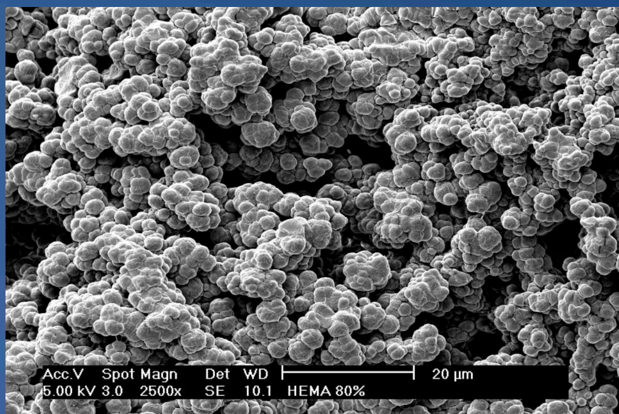


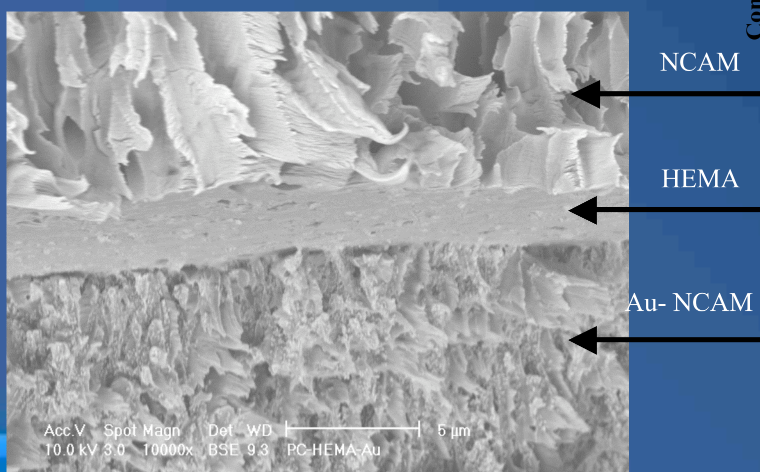
Schematic diagram representing the electrical double layer structures and potential profiles within nanopores at the extreme conditions where (A) κa > 1 and (B) κa < 1.

Paula J. Kemery, Jack K. Steehler, and Paul W. Bohn *Langmuir*, **1998,** *14(10)*, 2884.

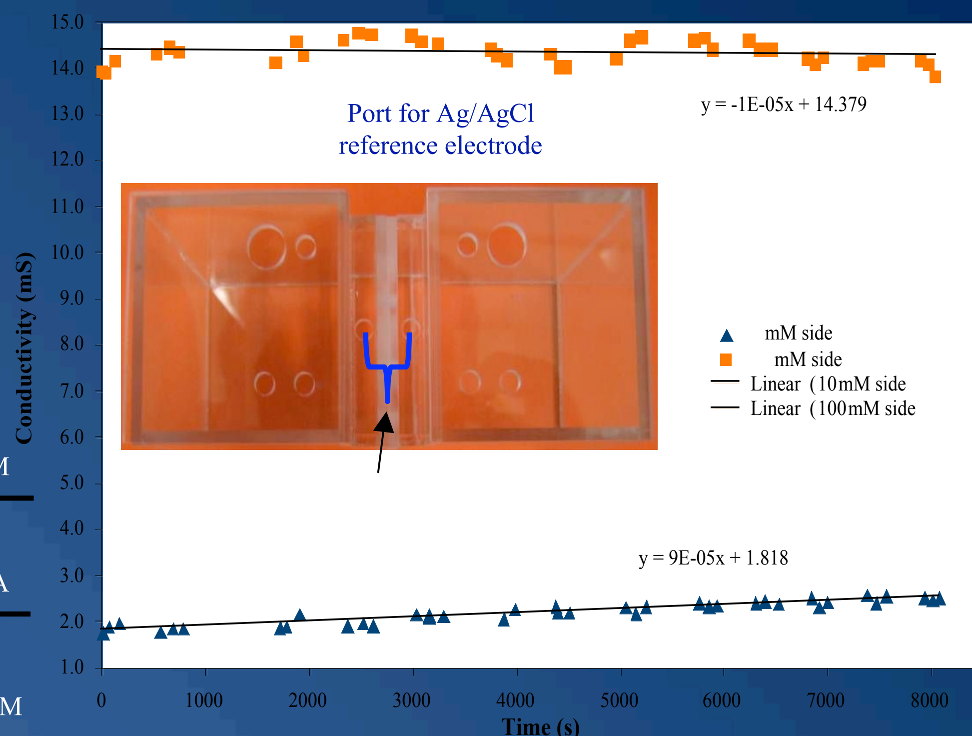
- Ionic strength adjusts ka
- At ka << 1 electroosmotic flow dominates
- At ka >> 1 ion migration dominates

Active Membrane System - Key Dimensions are < 1 nm to 100 nm!





Assembled 3-layer stack



Prakash, Rutgers
Shannon, UIUC

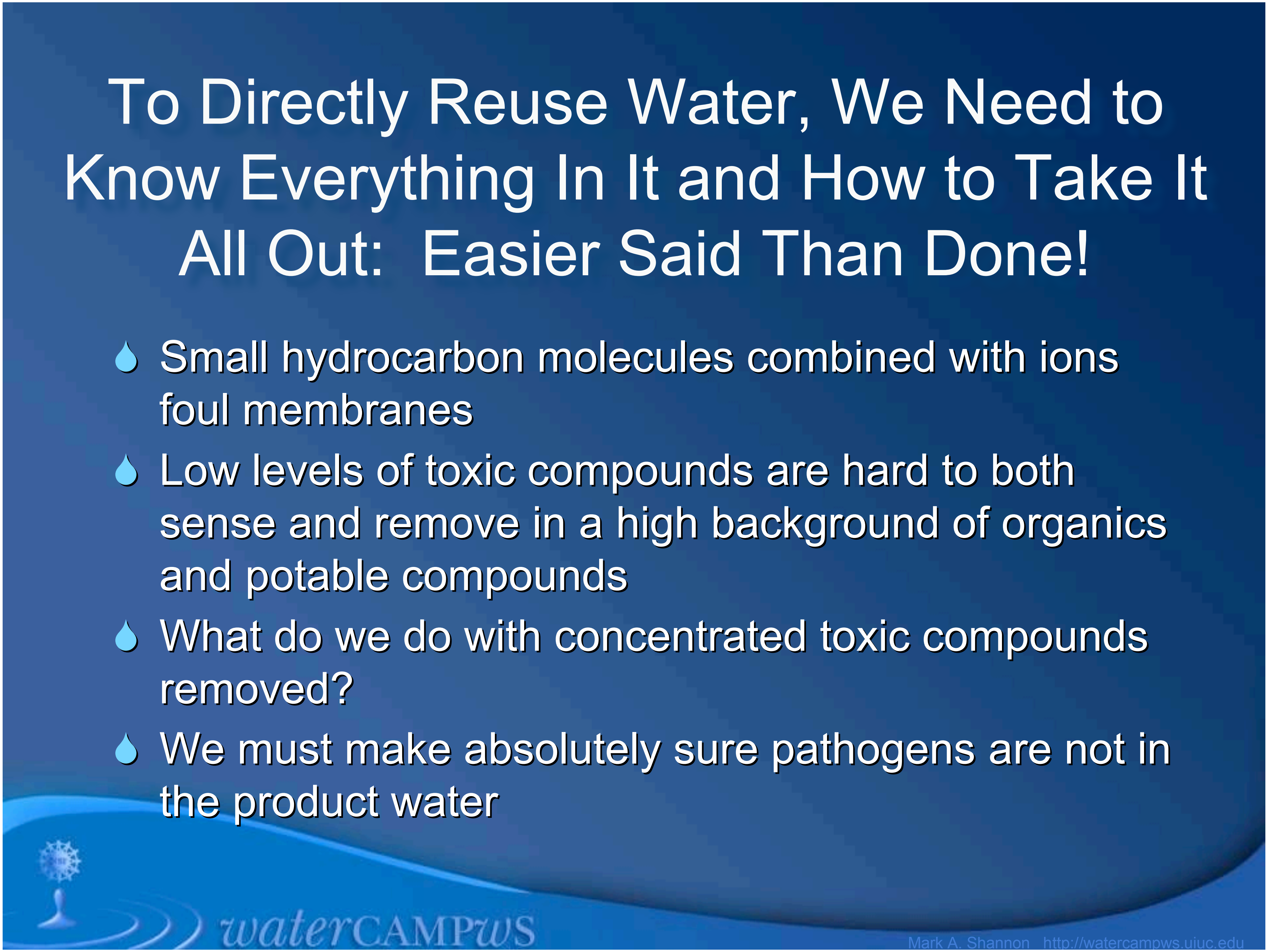
Recovery and Reuse of Water Creates an ENORMOUS RESOURCE

MEMBRANE BIOREACTORS **RO** **Disinfection (UV OR VISIBLE LIGHT)**

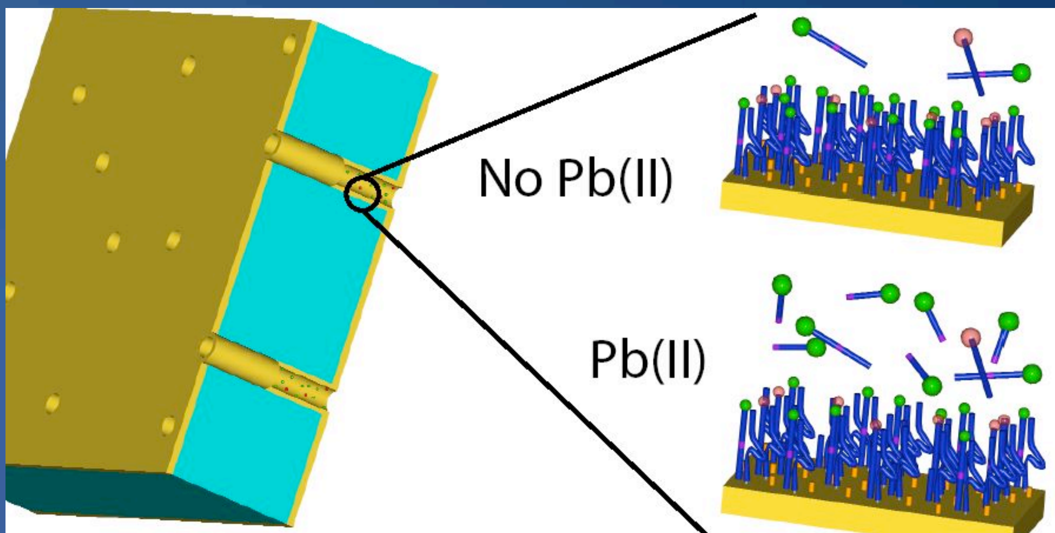
Wastewater Effluent →  →  →  → **Purified Water**

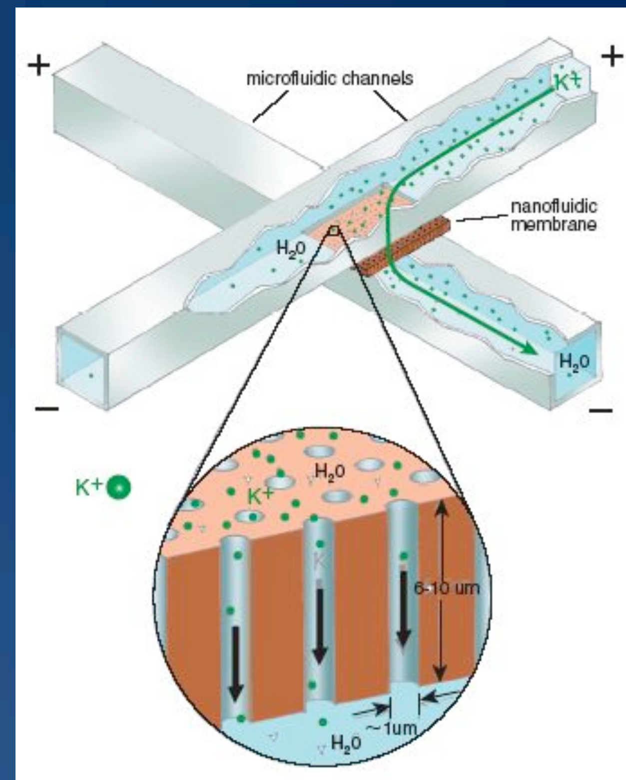
But how do we :

- Reduce energy and cost of reuse and desalination
- Ensure absolutely the highest quality and safety
- MBR’s can generate energy, instead of current goal of converting everything to CO_2, H_2O, and N_2


To Directly Reuse Water, We Need to Know Everything In It and How to Take It All Out: Easier Said Than Done!
Small hydrocarbon molecules combined with ions foul membranes
Low levels of toxic compounds are hard to both sense and remove in a high background of organics and potable compounds
What do we do with concentrated toxic compounds removed?
We must make absolutely sure pathogens are not in the product water
waterCAMPWS
Mark A. Shannon http://watercampws.uiuc.edu

Utilizing Catalytic DNA in Molecular Gates to Sense Trace Amounts of Lead





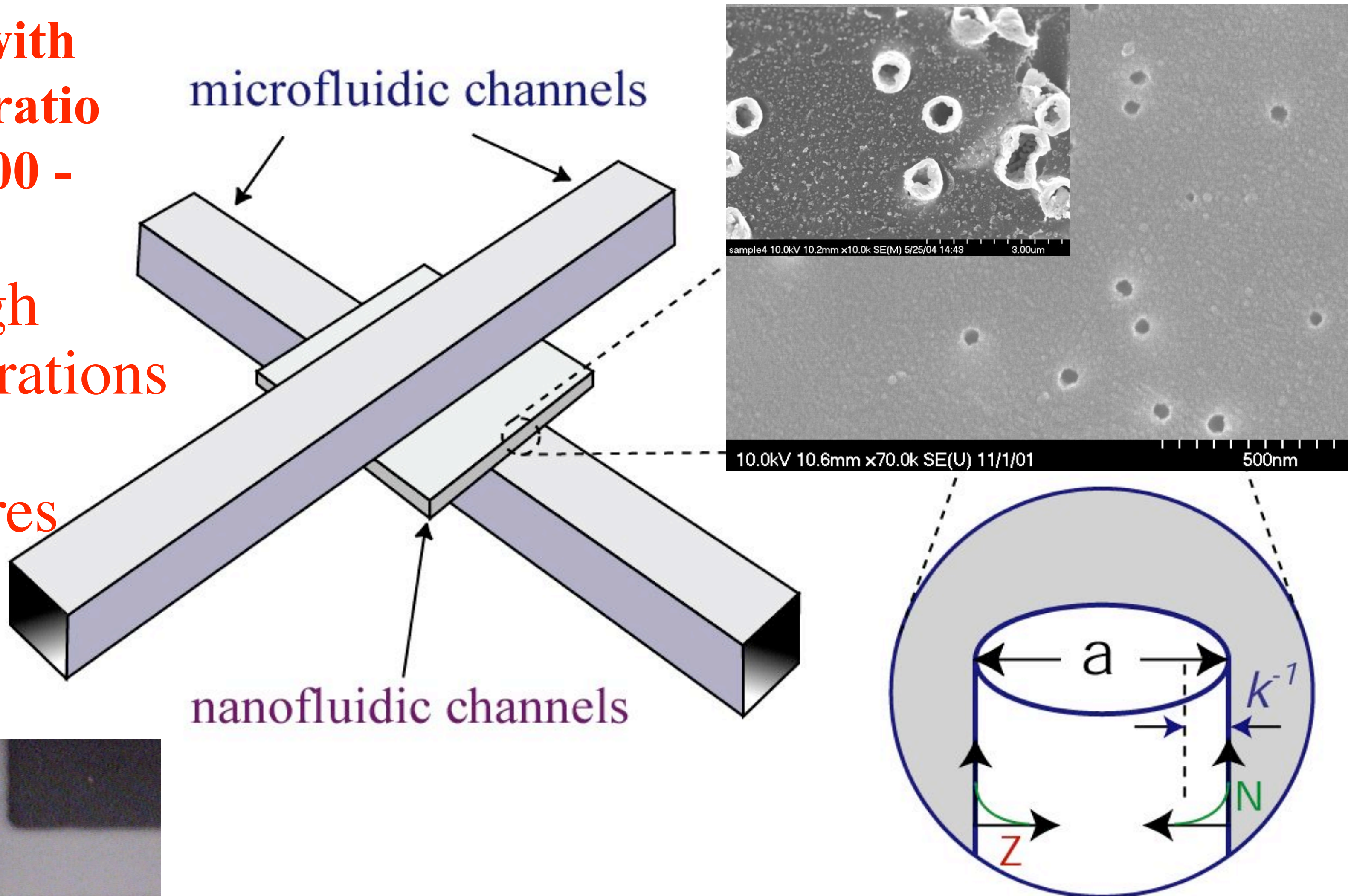
Molecular gate is a new ***micro-nanoscale*** construct that controls fluid molecules like electronic devices control electrons.

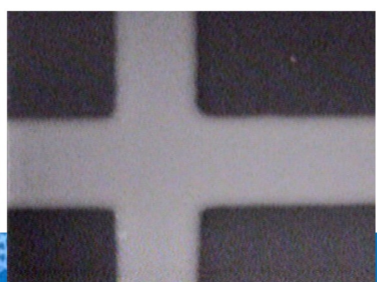
D. P. Wernette, C. B. Swearingen, D. M. Cropek, Y. Lu, J. V. Sweedler, and P. W. Bohn, *Analyst* 131, 41-47 (2006).
D. P. Wernette, C. Mead, P. W. Bohn and Y. Lu, *Langmuir*.

Micro/Nano Interconnect Creates a Gate

Pores with aspect ratio from 100 - 1000

very high concentrations within nanopores





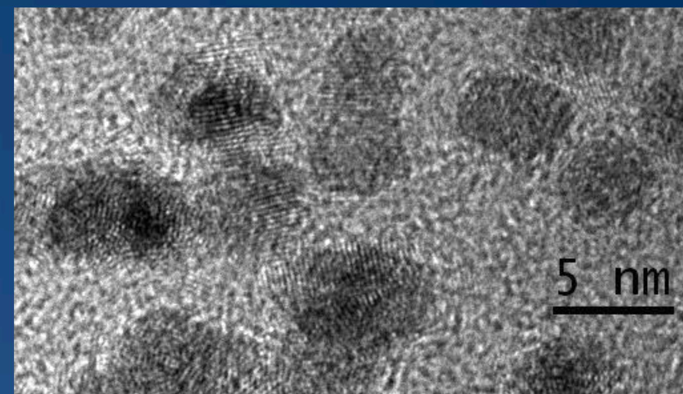
Zepto- (10^{-21}) to Attoliter (10^{-18}) volumes

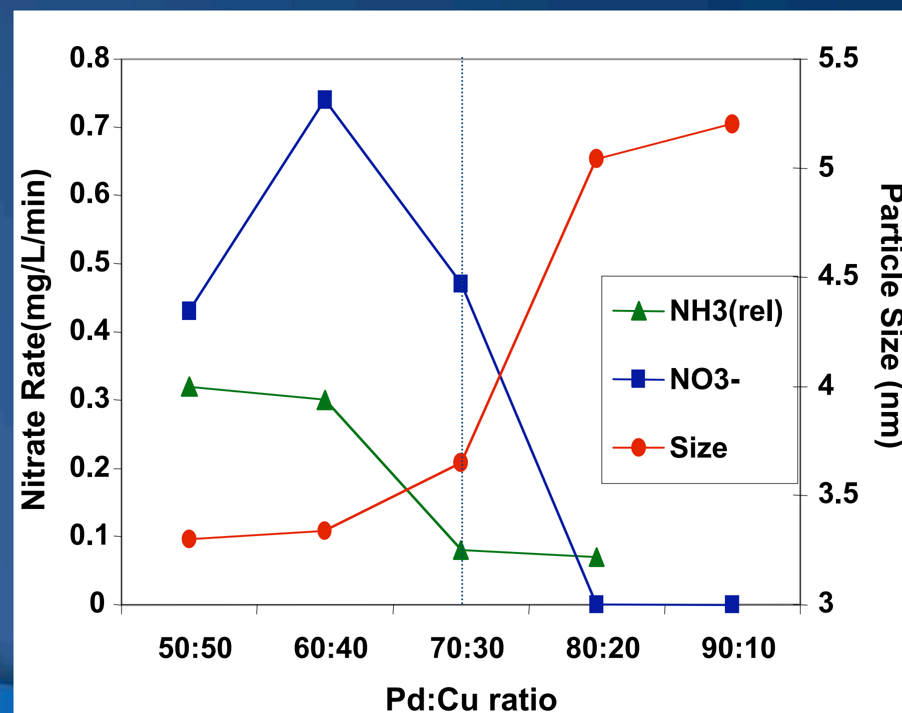
Using Nanocatalysts to Transform Nitrates and Perchlorates to Harmless Compounds

- Catalytic studies show strong change in reaction rate and selectivity that correlates with change in nanoparticle size and composition.

Guy, Chaplin, Shapley, Werth, UIUC

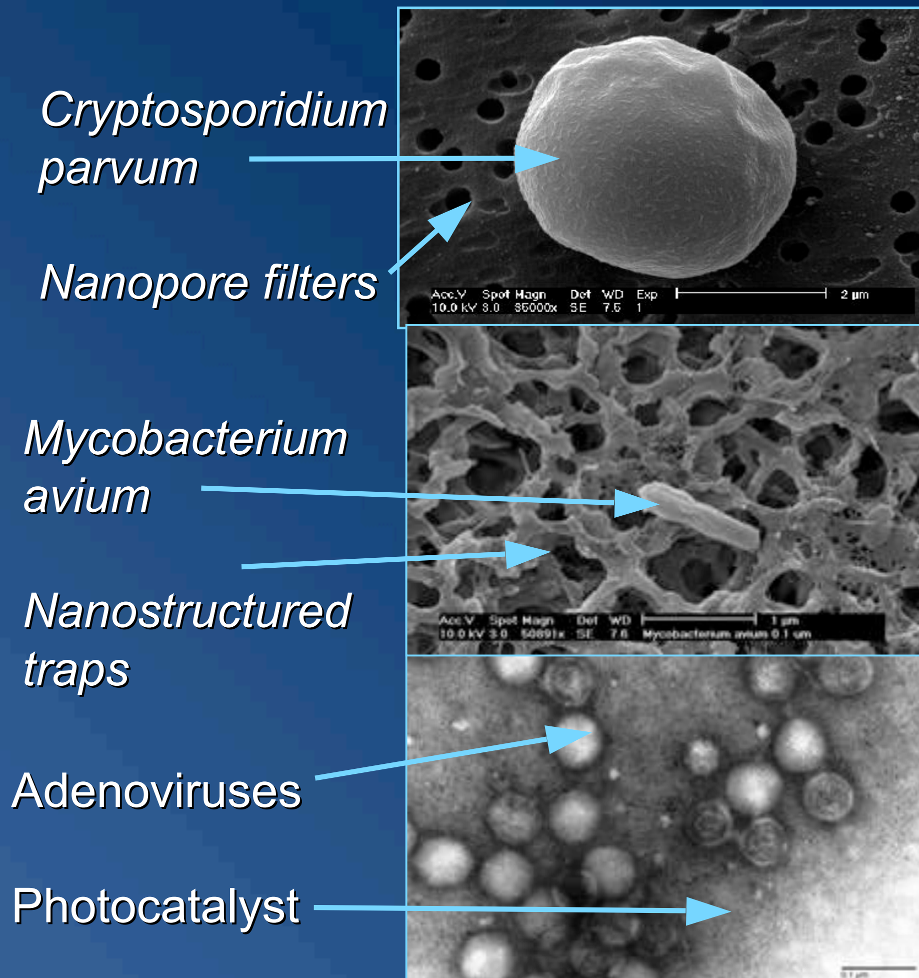
Xu, Yang, U. Pittsburgh





Disinfection of Hard to Treat Pathogens, Without Intensive Chemical Treatment

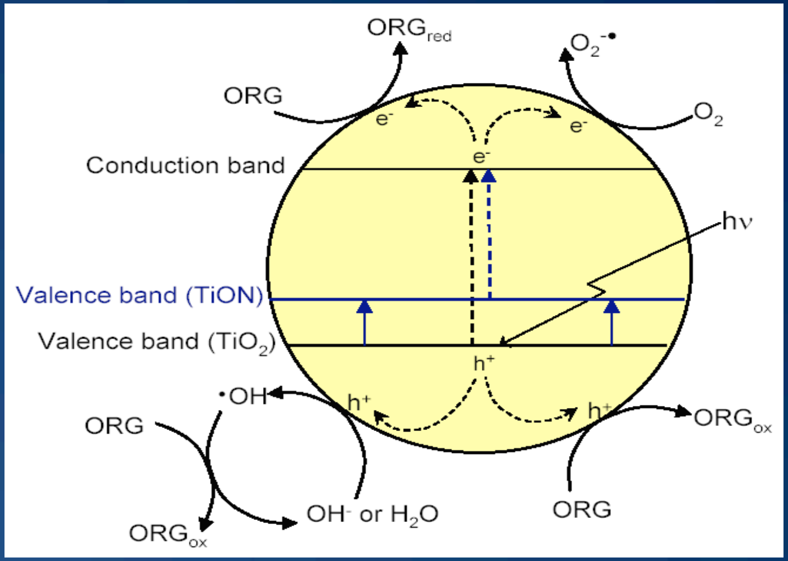
Use of nanostructured membranes and particles, catalysts, and photocatalysts and light to inactivate pathogens in water, without using chlorine or other powerful oxidants that can themselves form toxic compounds.



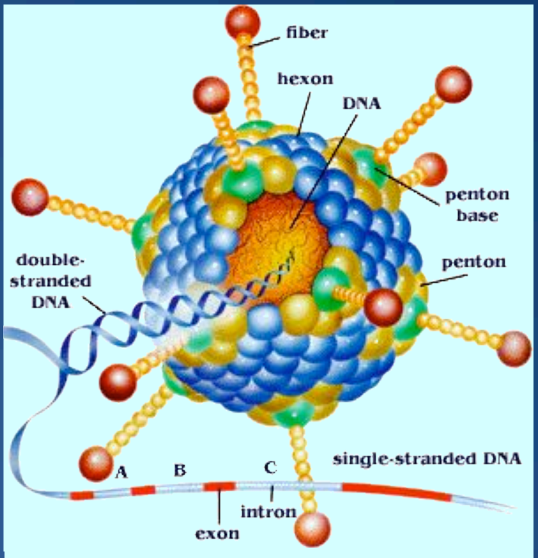
Benito Mariñas, UIUC

Kill Pathogens with Plentiful Light

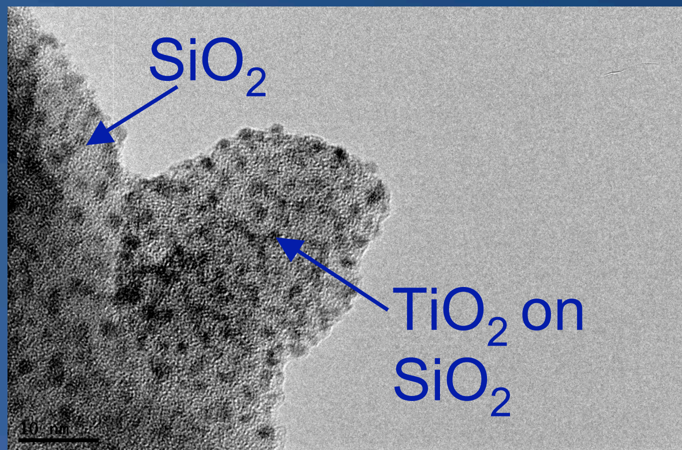
- Making highly effective and selective photocatalytic technologies that on nanoparticles can inactivate pathogens from hard to treat oocytes and spores, to viruses



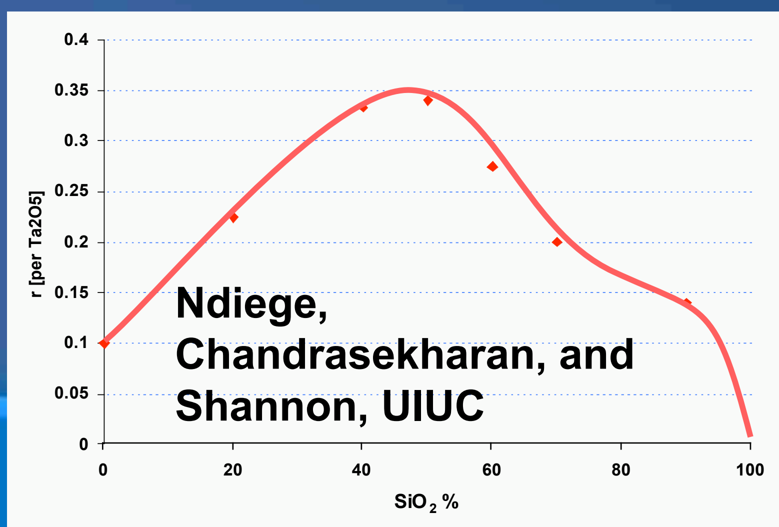
Adenovirus



Photocatalysis Can Perform Better and Cost Less at the Nanoscale!



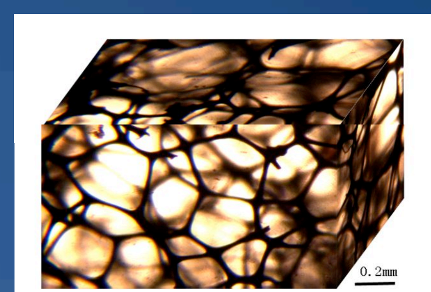
TEM micrograph of 2 nm diameter TiO_2 on 20 nm diameter SiO_2 particles

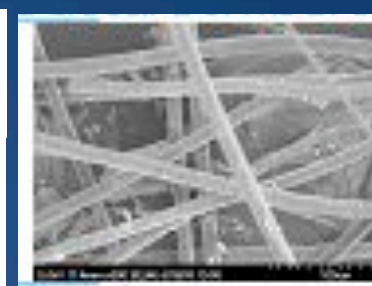


– Nanopowders

TiON M/TiON

– Templated M/TiONporous structures/fibers





Jian-Ku Shang, James Economy, UIUC

What Can We Do?

- Help set a Strategic Plan for future water science and technology. The *U.S. Strategic Water Initiative* (USSWI) seeks to establish a set of R&D programs: USSWI Congress in New Orleans April 6-12, 2008
- Drive governments, NGO’s, industries, water suppliers and users input into strategic planning process
- Develop Public/Private Partnership: Funding does not have to be purely governmental.
- Build infrastructure to move bold new ideas into practice, appropriate for each region of the world.

WE NEED A RESEARCH PIPELINE TO MOVE NANOWATER TECHNOLOGIES FORWARD

A Future Water-based Economy?

- The worldwide market for water purification technologies will be in the trillions in the next two decades.
- Water is already unaffordable for billions.
- Who is going to pay for the technological solutions it needs?
- If water is the oil of the 21st century, who will command the world market place for water and solutions? How can this be equitable for people from all walks of life?