

A graphic of a water splash in the top left corner, with water droplets and a stream of water falling from a point.

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

Impact of Water on Sustainability: Nexus to the Economy, Energy and Environment

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University of Illinois

A graphic of a water splash in the bottom right corner, showing a water droplet hitting a surface and creating concentric ripples.

waterCAMPWS

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
- 9 universities, 6 partners, 12 industrial affiliates, ~120 students, ~50 faculty



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 the vital role that people from all walks of life, can do to help solve these problems.



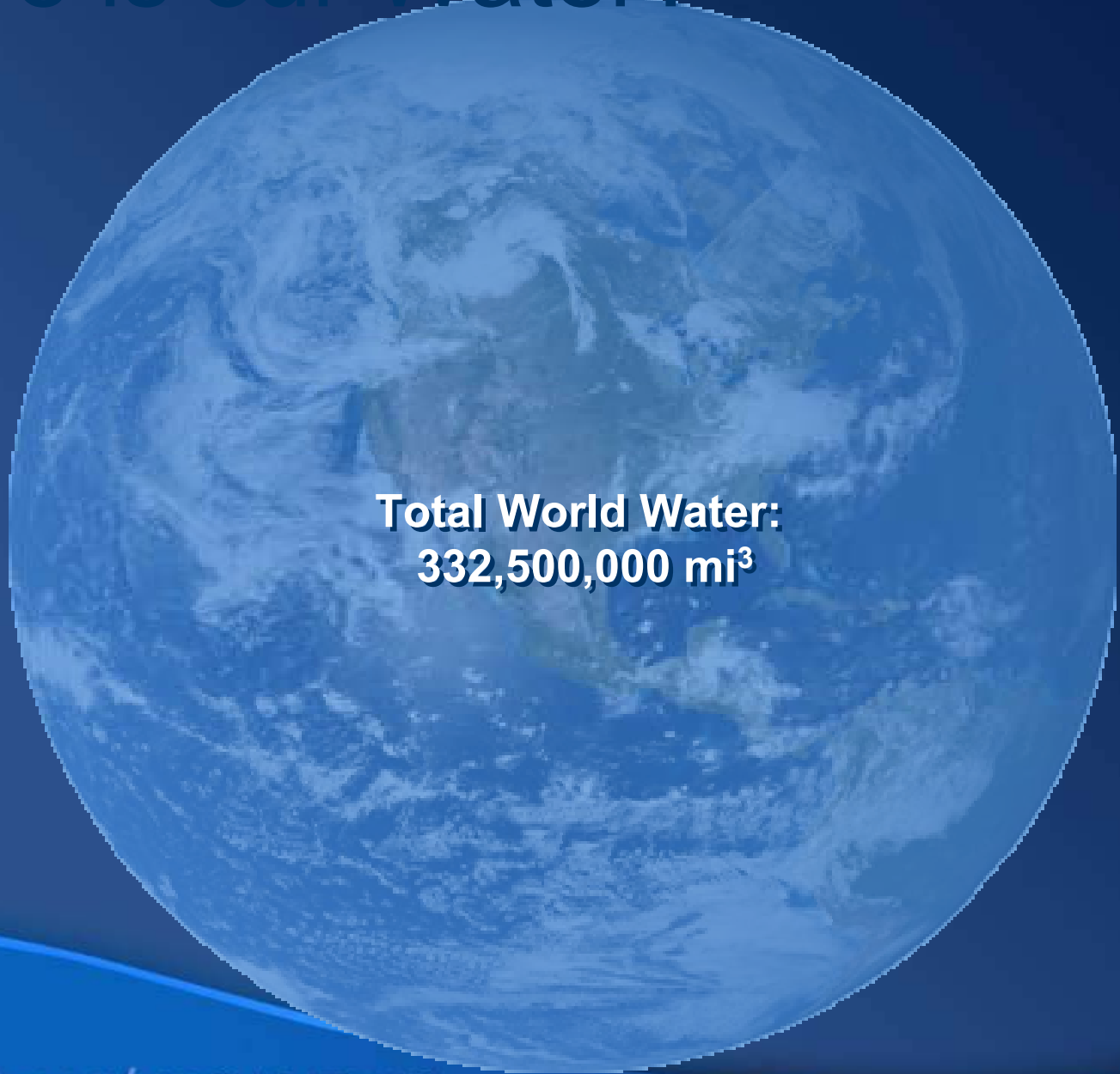
Value of Water

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

**HARD TO OVERESTIMATE IMPORTANCE,
BUT TAKEN FOR GRANTED BY MOST IN U.S.**



Where is our Water?



**Total World Water:
332,500,000 mi³**



Where is our Water?

Ice Caps, Glaciers, & Perm. Snow
1.74%
5,773,000 mi³
(68.7% fresh)

Ground Ice & Permafrost
.022%
71,970 mi³
(.86% Fresh)

Saline Lakes
.006%
20,490 mi³

Saline Groundwater
.94%
3,088,000 mi³

Accessible With Additional Research

Oceans, Seas, & Bays
96.5%
321 million mi³

Currently Accessible for Human Use
30% shortfall in 30 yrs

Lakes
.007%
21,830 mi³
(.26% fresh)

Rivers
.0002%
509 mi³
(.006 Fresh)

Groundwater
.76%
2,526,000 mi³
(30.1% fresh)

Atmosphere
.001%
3,095 mi³
(.04% Fresh)

Biological
.0001%
269 mi³
(.0036% Fresh)

Swamps
.0008%
2752 mi³
(.03% fresh)

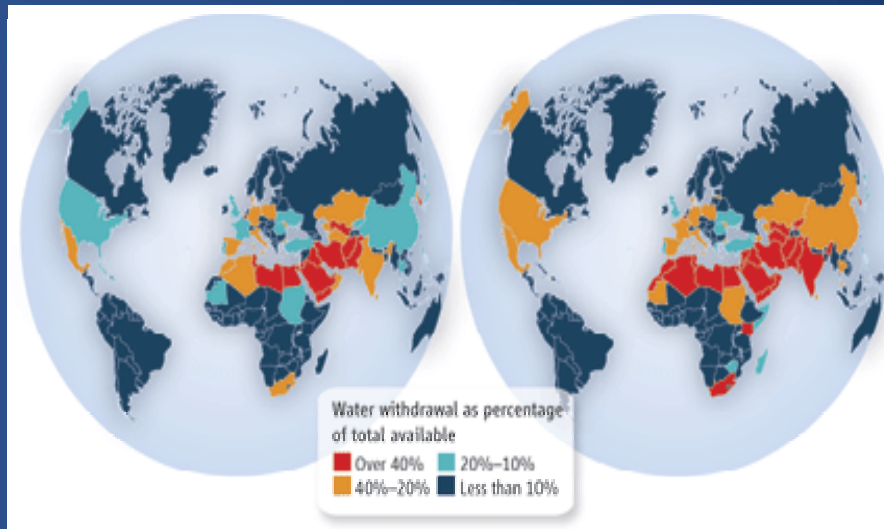
Soil Moisture
.001%
3,959 mi³
(.05% Fresh)

99.23% currently unusable for most humans

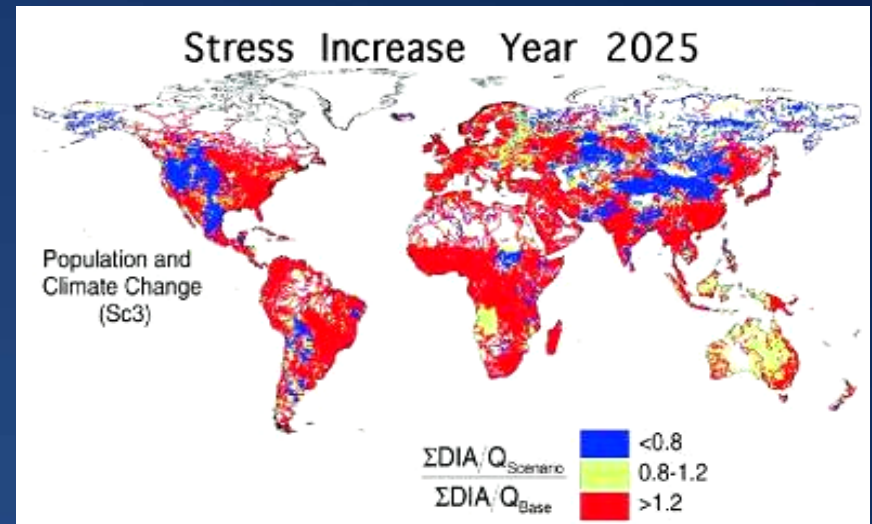


Major Problems Facing World

- 💧 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.

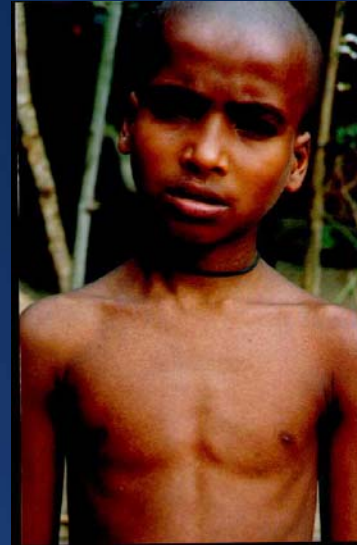


World Map showing affect of population and climate change on water stress.



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
- 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

Standard Aquifers

> 20% and growing

Aluvial and Glacial

~ 10% but not
replenishable

Reservoirs

Increase storage, but
increase losses

water is local to the
watersheds, but they
are interconnected

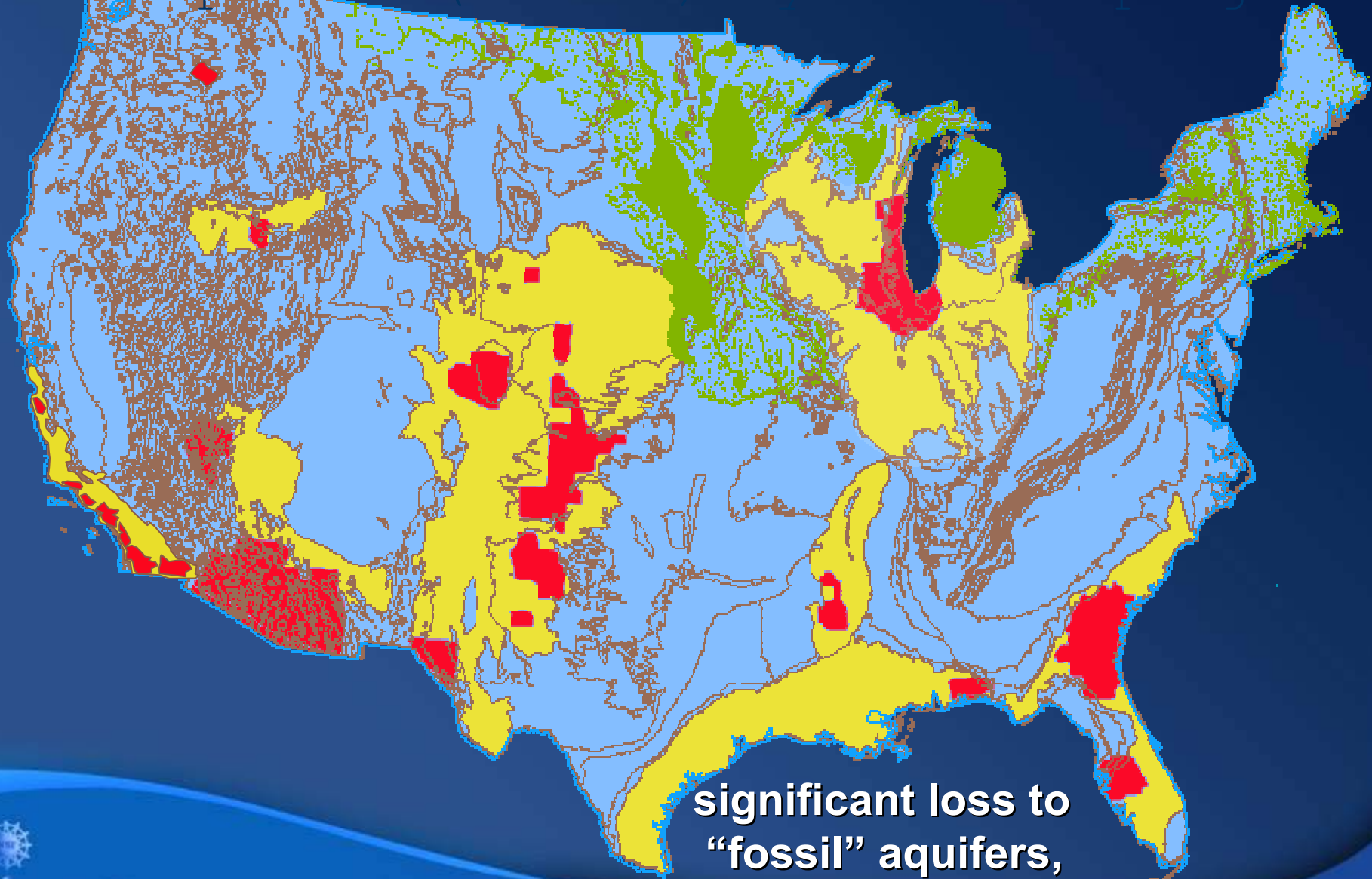
U.S. Department of the Interior
<http://www.nationalatlas.gov>



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Mark A. Shannon <http://watercampus.uiuc.edu>

Aquifers - Currently Stressed (Red) and Impacted (Yellow) by Over-Pumping



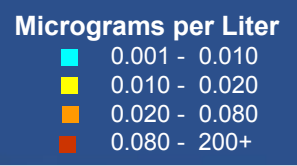
significant loss to
“fossil” aquifers,
south, southwest, and heartland

High Critical Drinking Water Contaminants and Salts in Surface and Groundwaters

Water Treatment:
Repeated treatments
increases salting and
purification costs

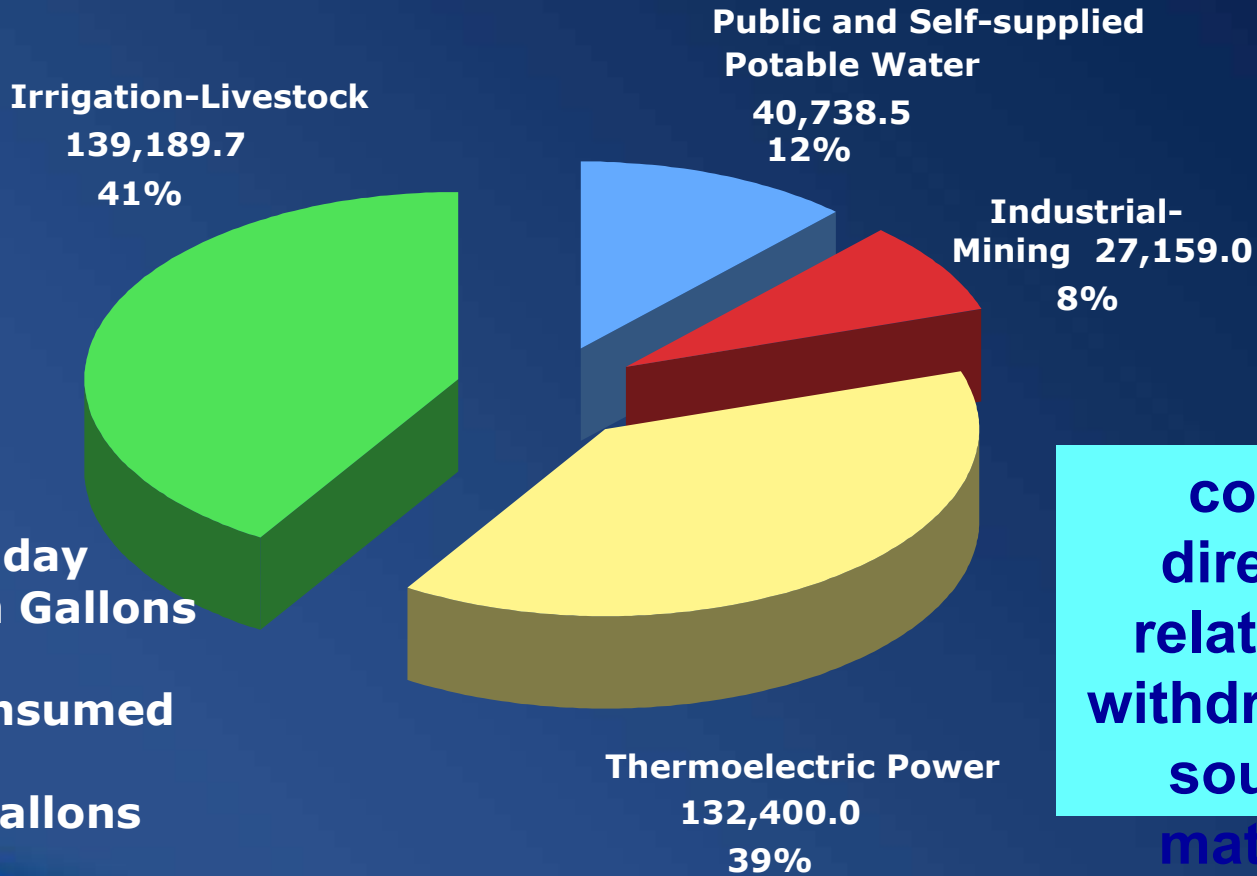
salting from
pumping and surface
runoff: Mexico issues

contaminates
growing in amounts,
types, and population



Volume of Water Withdrawn for All Uses

(Million Gallons per Day)



costs directly related to withdrawals: source matters

Total Water Withdrawn per day
339,487 million Gallons

Total Water Consumed per Year
123.9 Trillion Gallons



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

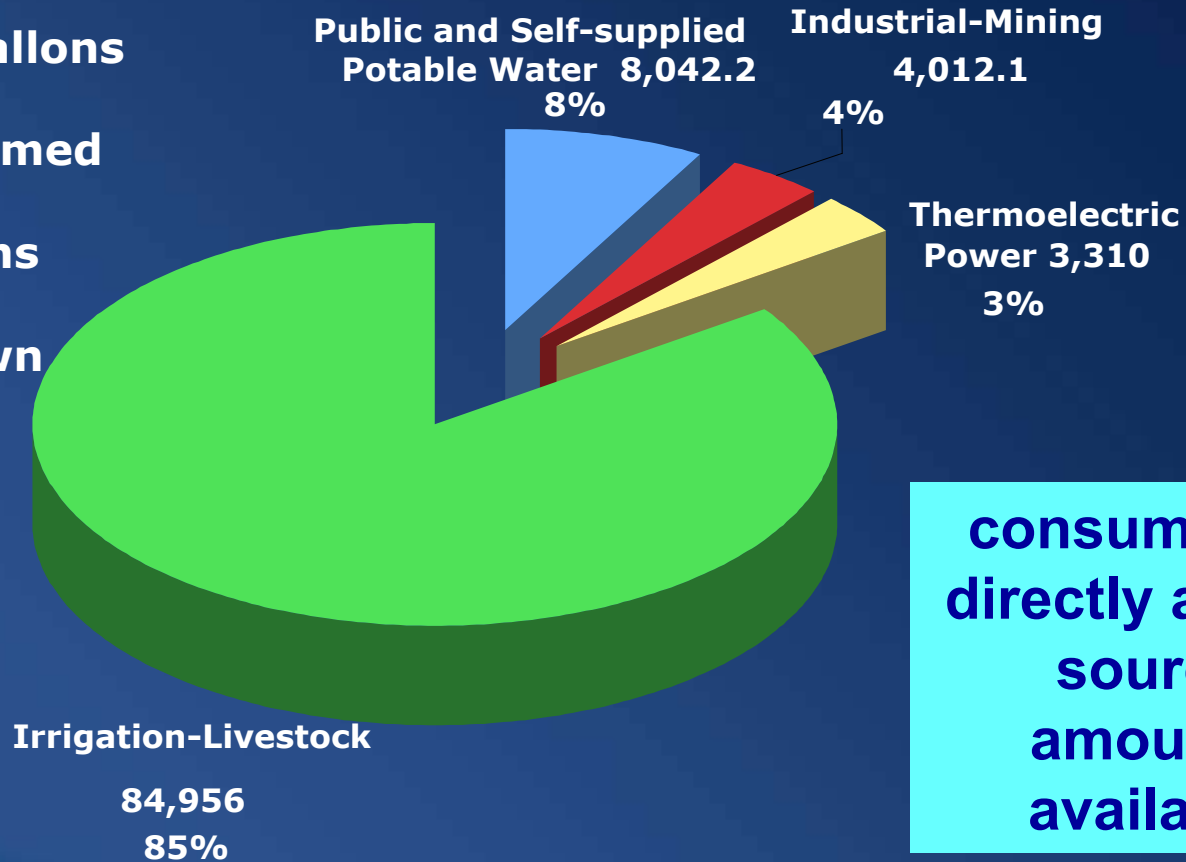
Volume of Water Consumed

(Million Gallons per Day)

Total Water Consumed
per day
100,320 million Gallons

Total Water Consumed
per Year
36.6 Trillion Gallons

~30% of withdrawn



**consumption
directly affects
source
amounts
available**



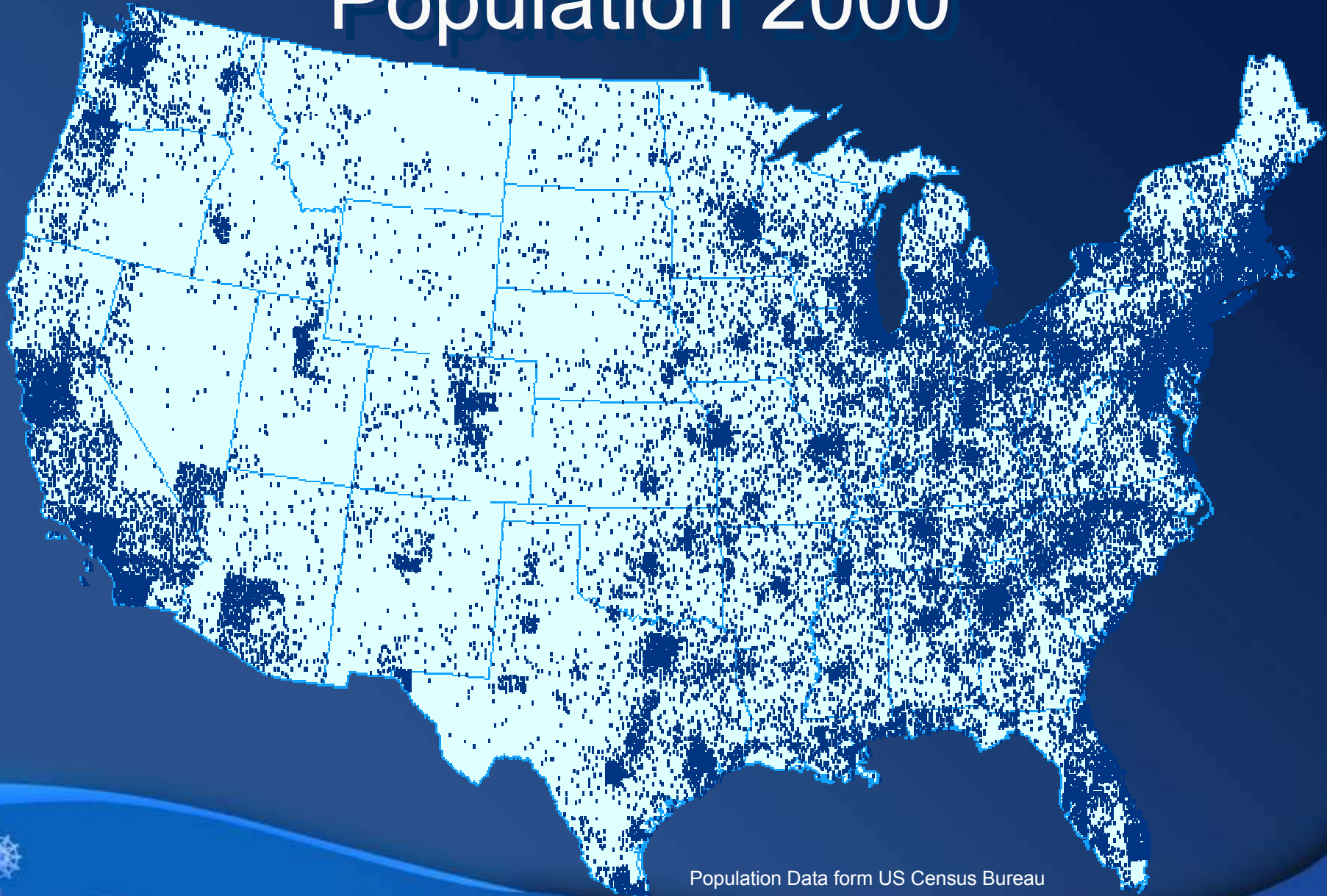
"Consumptive Water Use for U.S. Power Production,
P. Torcellini, *et.al.*, National Renewable Energy Laboratory, 2003.

Projections

- 💧 Population driven
- 💧 Application driven
- 💧 Source driven



Population 2000

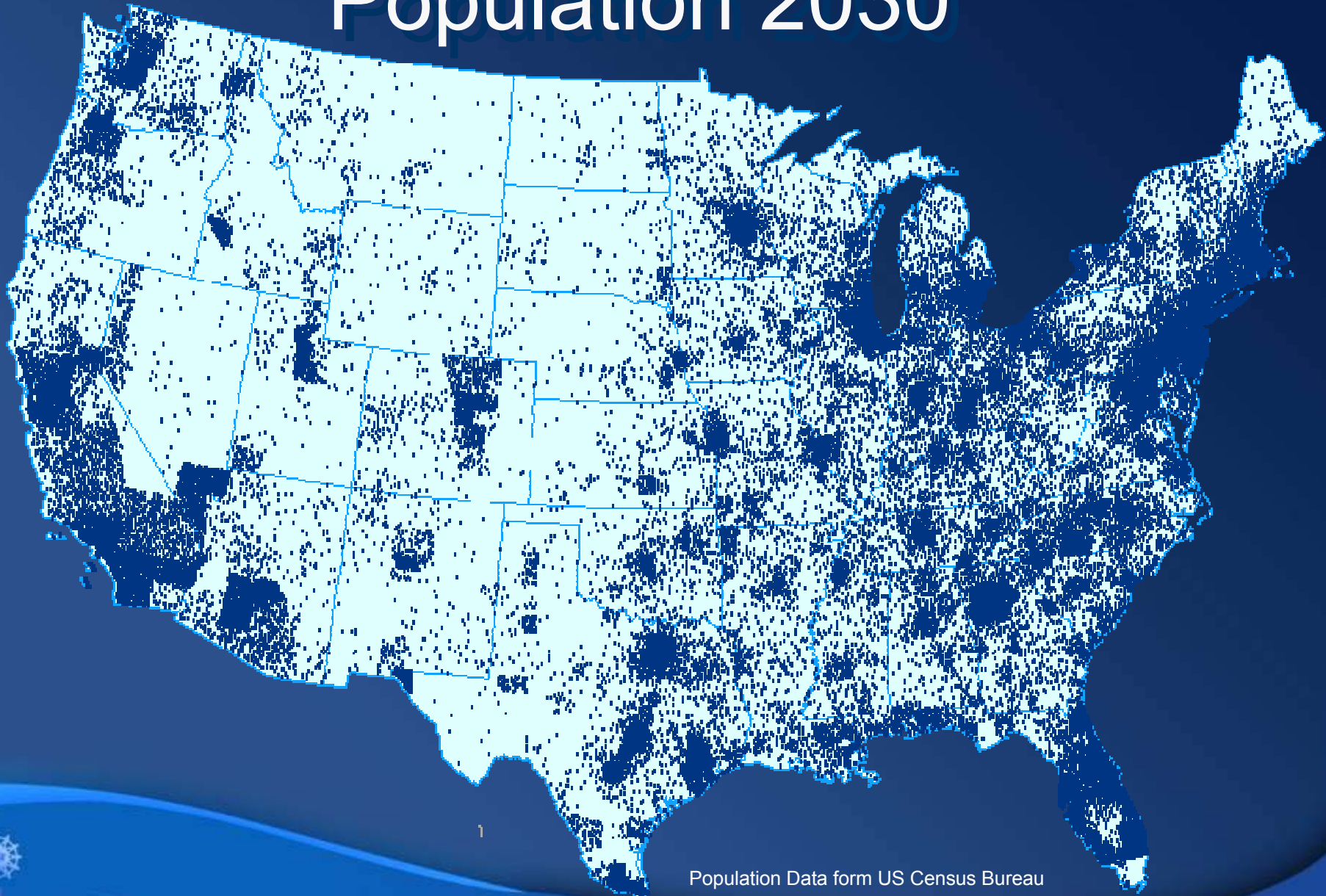


Population Data from US Census Bureau



waterCAMPus

Population 2030



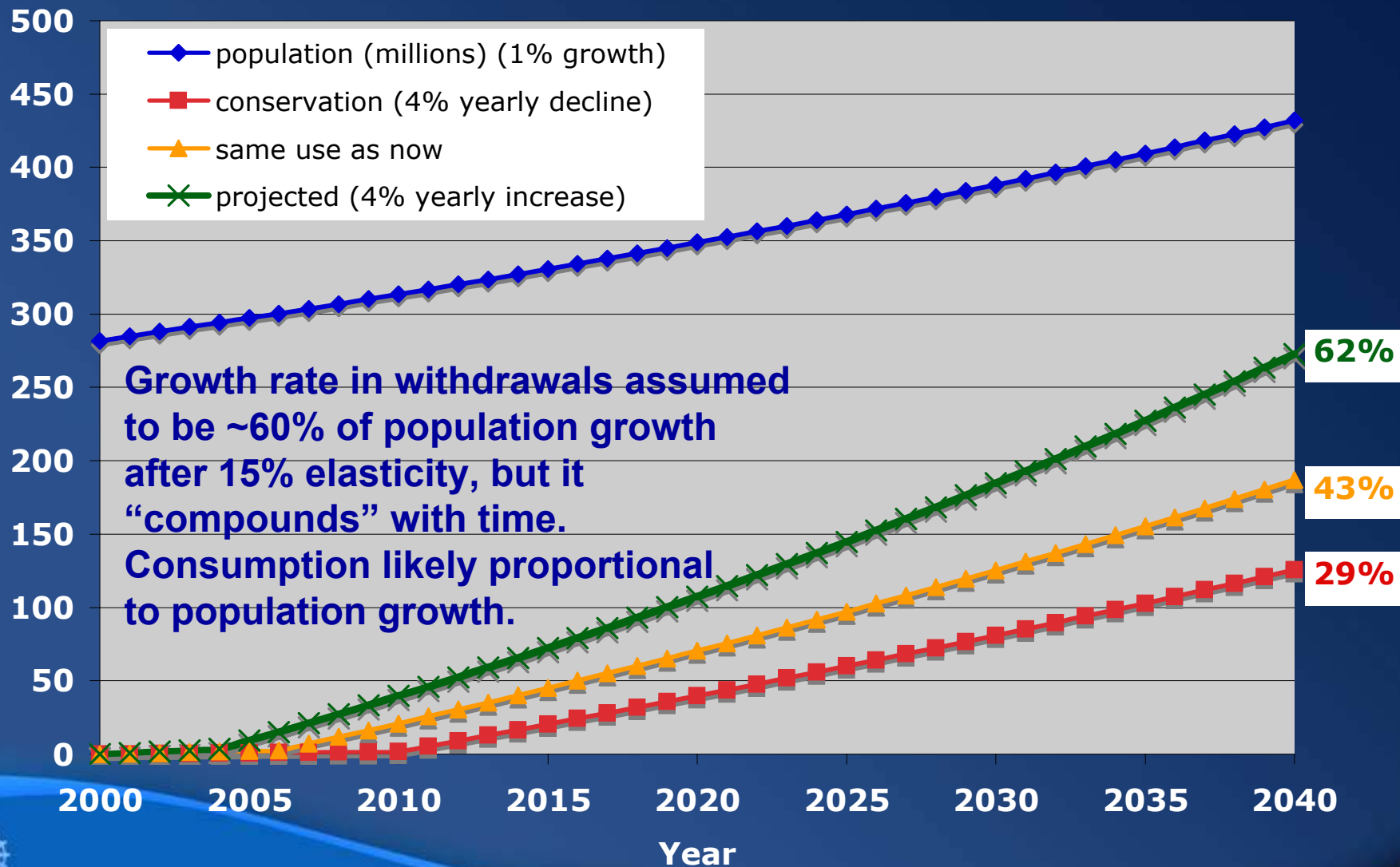
Population Data form US Census Bureau



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Water Use Growth With Population

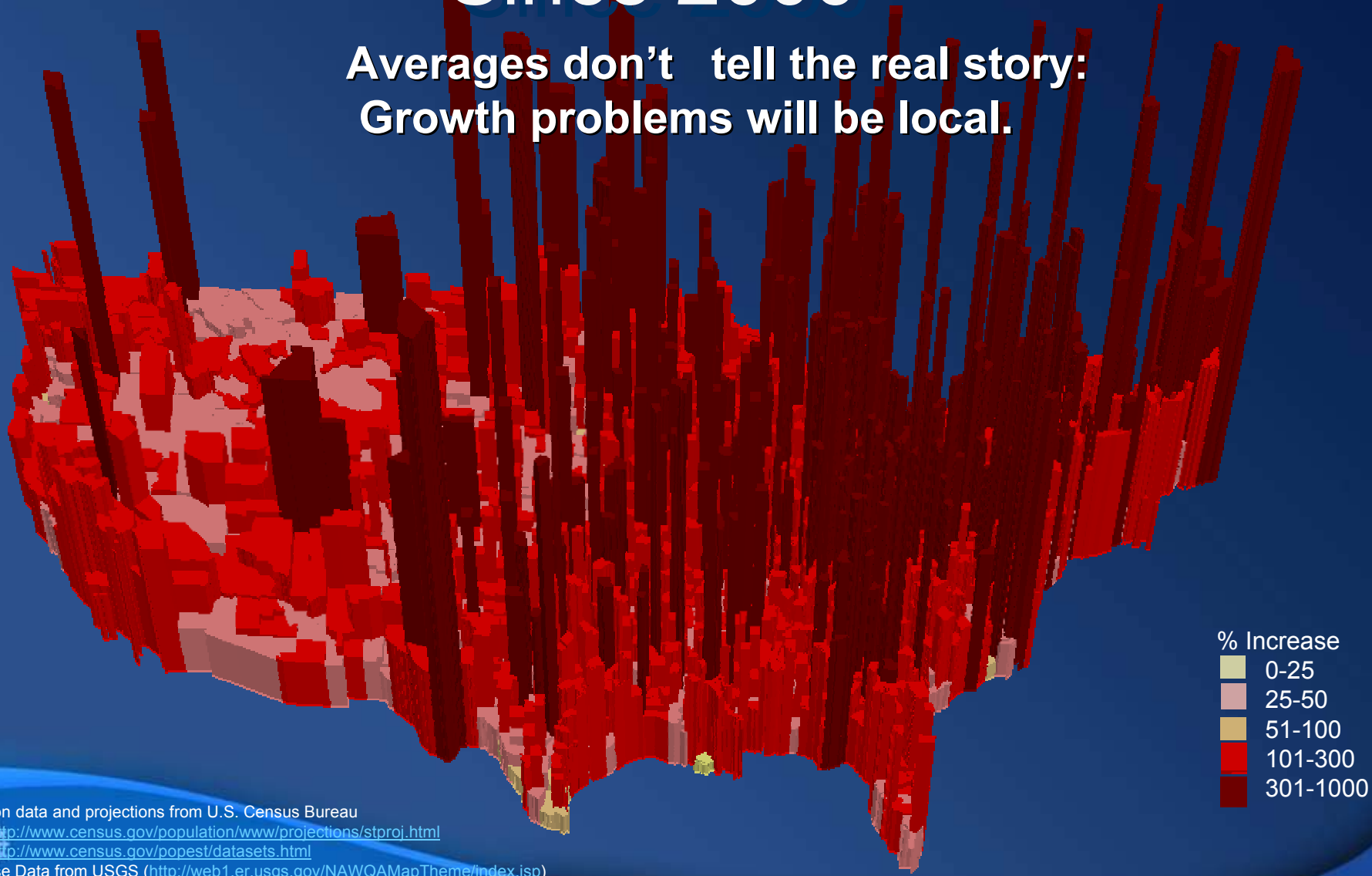
Increase in Million Acre Feet (325,500 gal) of Water Withdrawn



Population Data form US Census Bureau

2030 Projected Increase in % of Use Since 2000

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



% Increase

- 0-25
- 25-50
- 51-100
- 101-300
- 301-1000

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)

U.S. Economic Issues

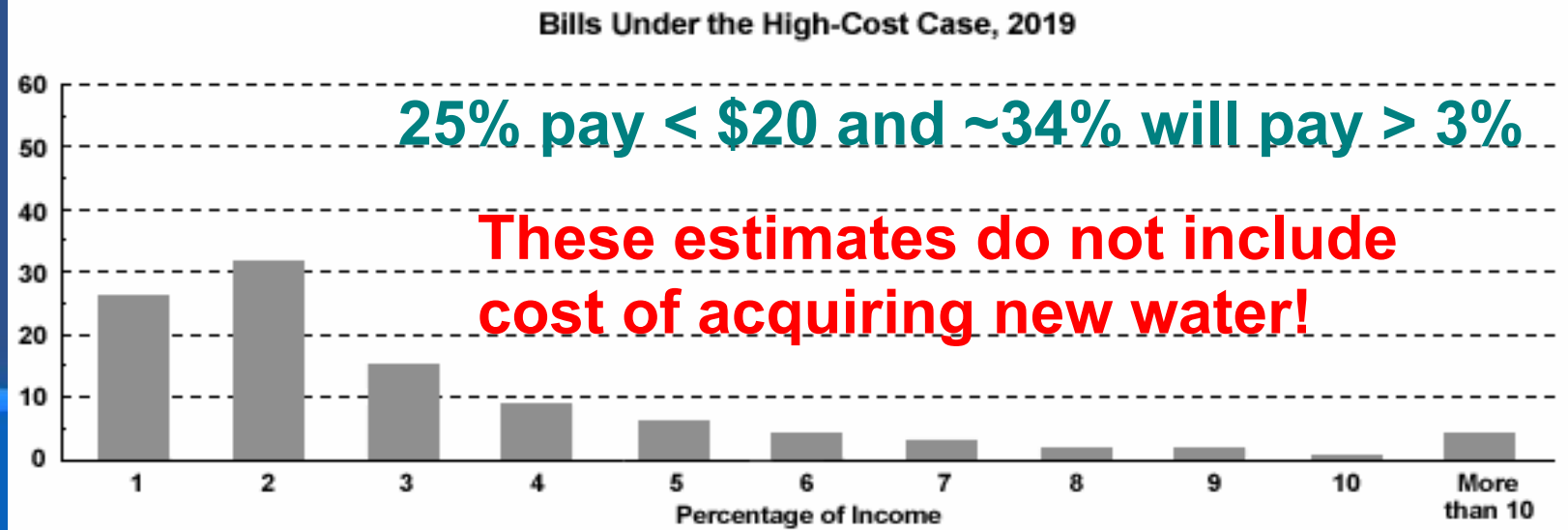
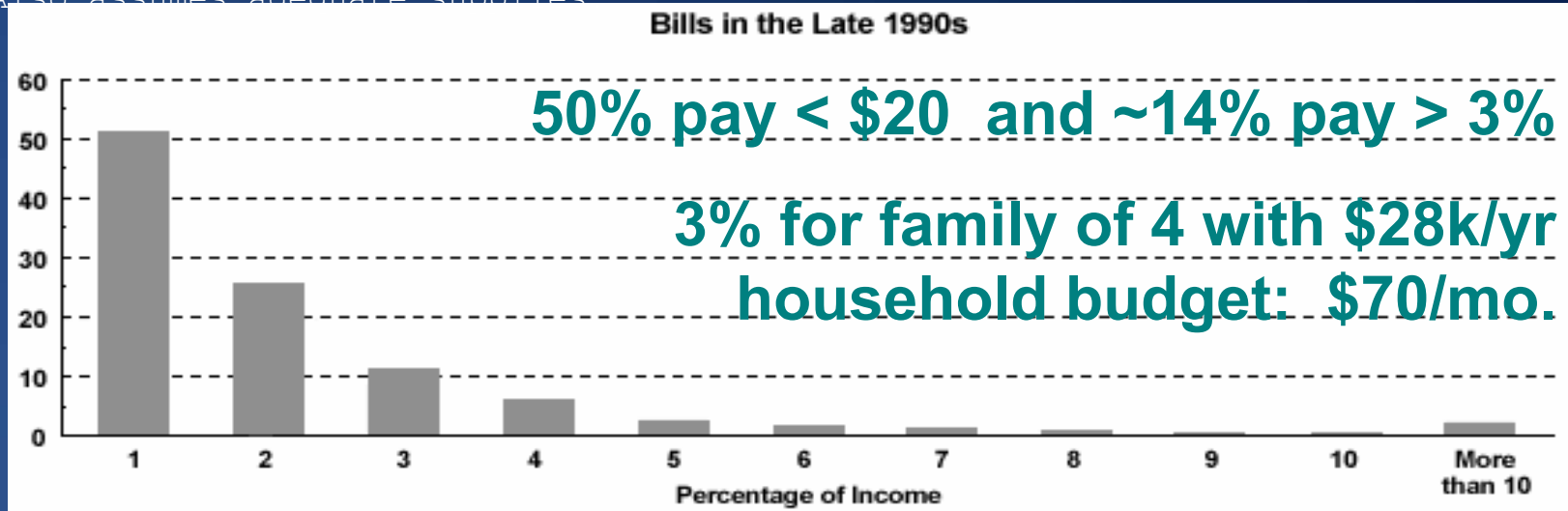
- More than \$1 trillion (2001 dollars) spent on water treatment, in past 20 years: \$10,000 invested in infrastructure for every American
- More than \$1 trillion (2001 dollars) more needed for infrastructure, and treatment in next 20 years
- Demand for potable water currently exceeds available resources in parts of U.S. New waters in next 35 years > \$2 trillion
- 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

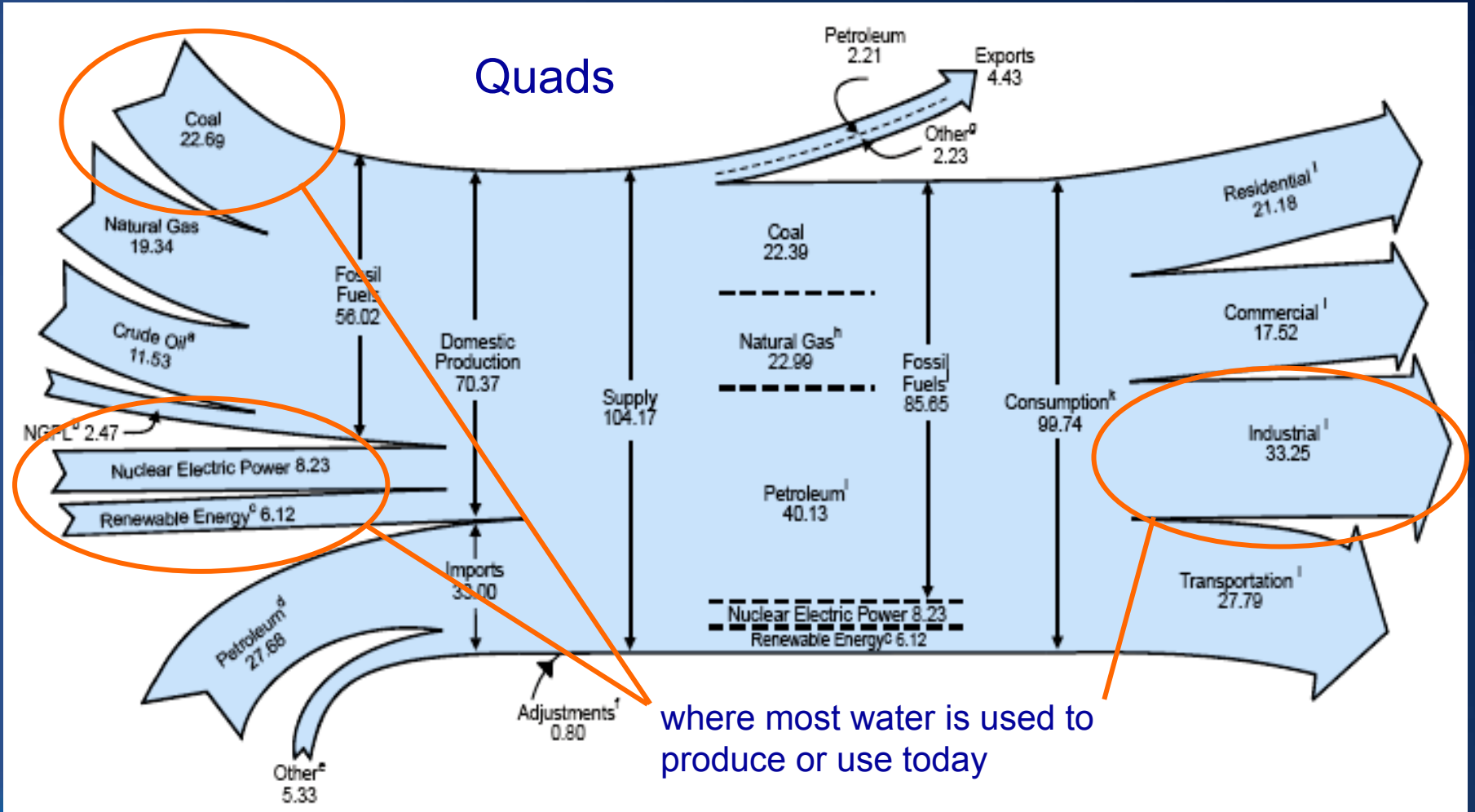


Effect on Consumer for Water Costs

CBO's estimates assume steady levels of support financed by taxpayers and constant shares of water costs paid by household and non-household ratepayers. Also assumes adequate supplies.



Flow of Energy in U.S.



Energy and Water

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
- We're the Saudi Arabia of Oil Shale, but we can't utilize it without lots of water
- Plug-in hybrid vehicles will be impacted, from restricted electric generation

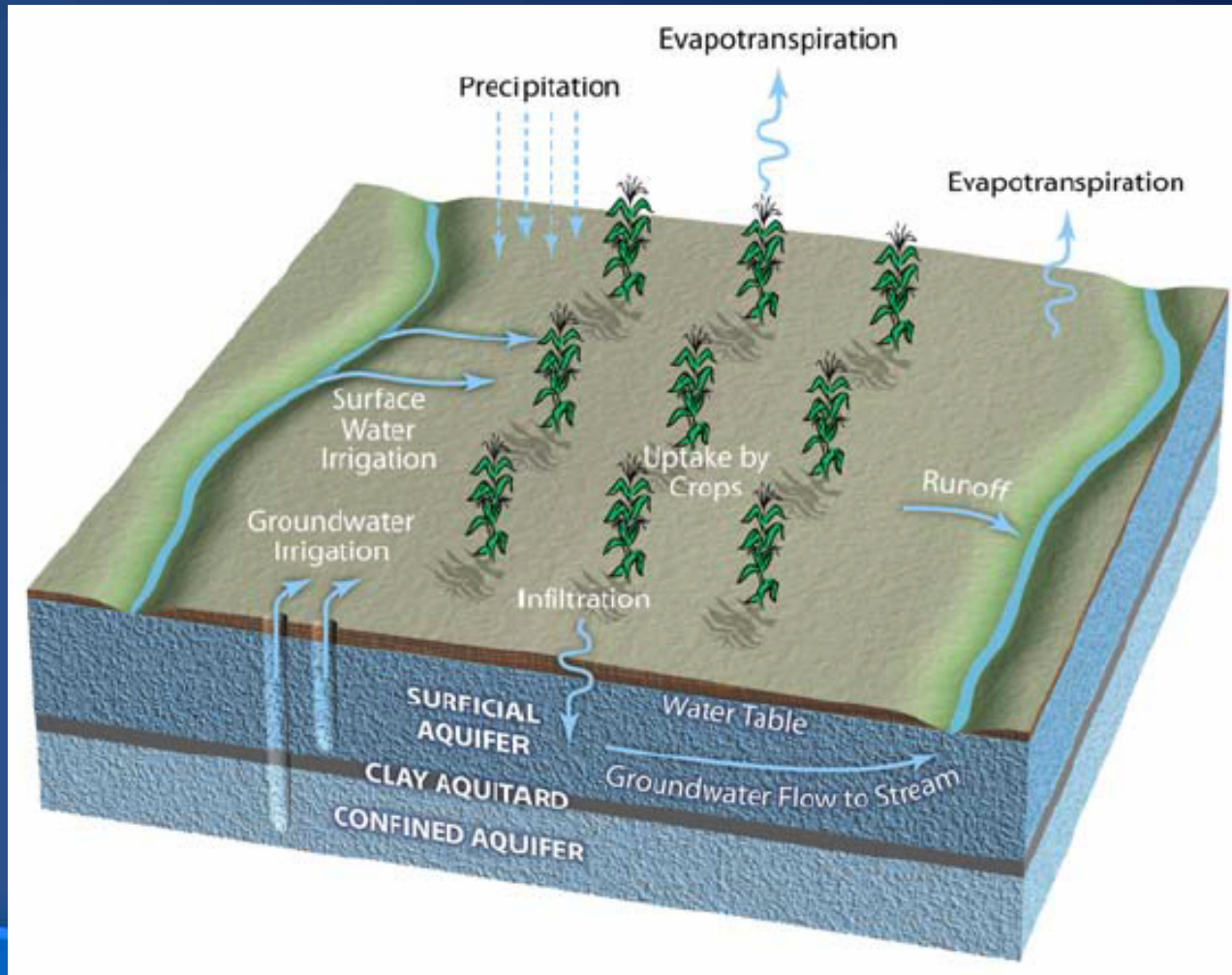
Without sufficient energy:

- We cannot supply sufficient clean water!



The Agricultural Water Cycle

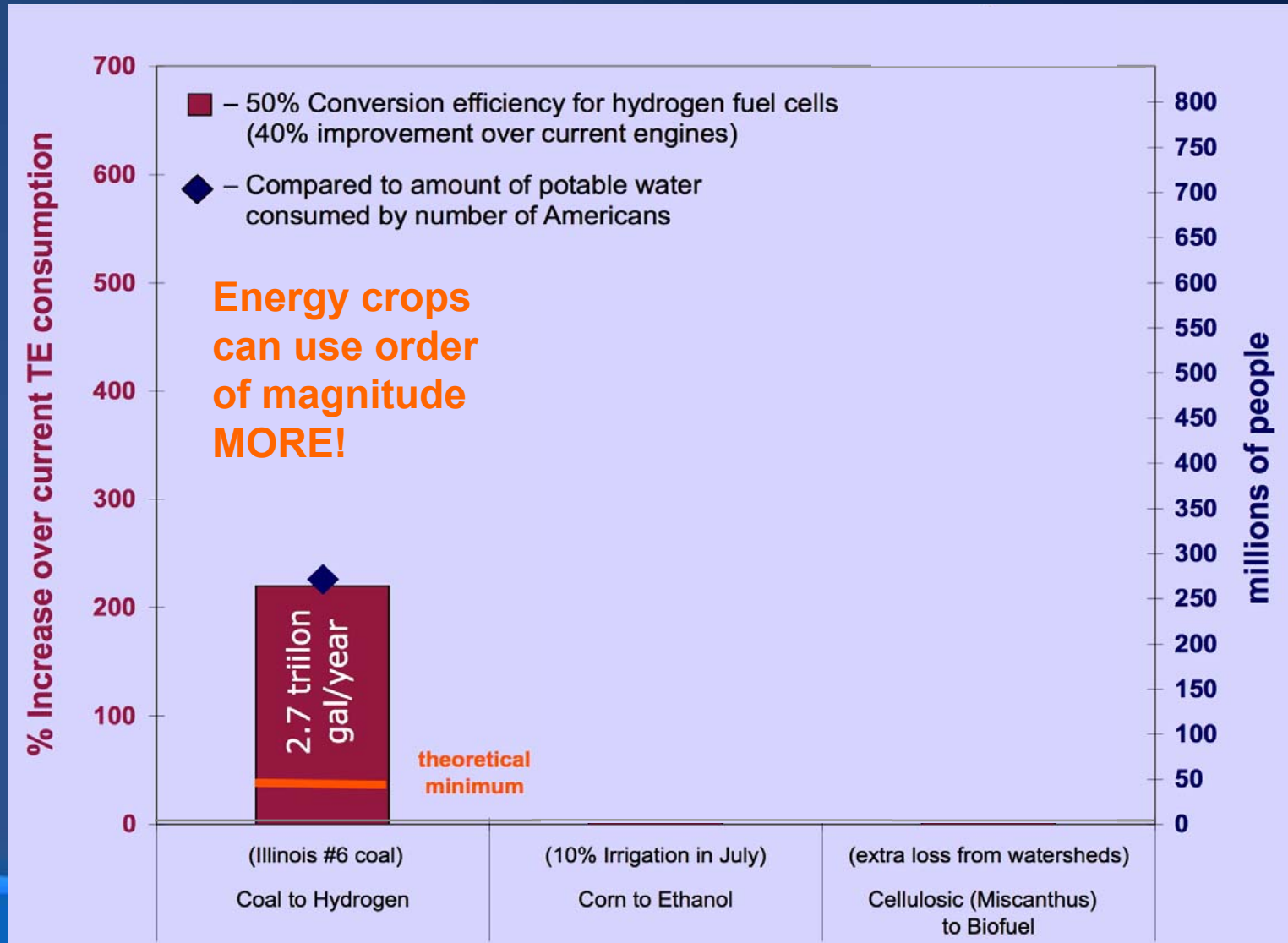
Inputs and outputs to a crop include rainfall and irrigation from surface water and groundwater, pan runoff and evaporation, infiltration, and evapotranspiration.



SOURCE: "Water Implications of Biofuels Production in the United States," National Academies Press (2007).

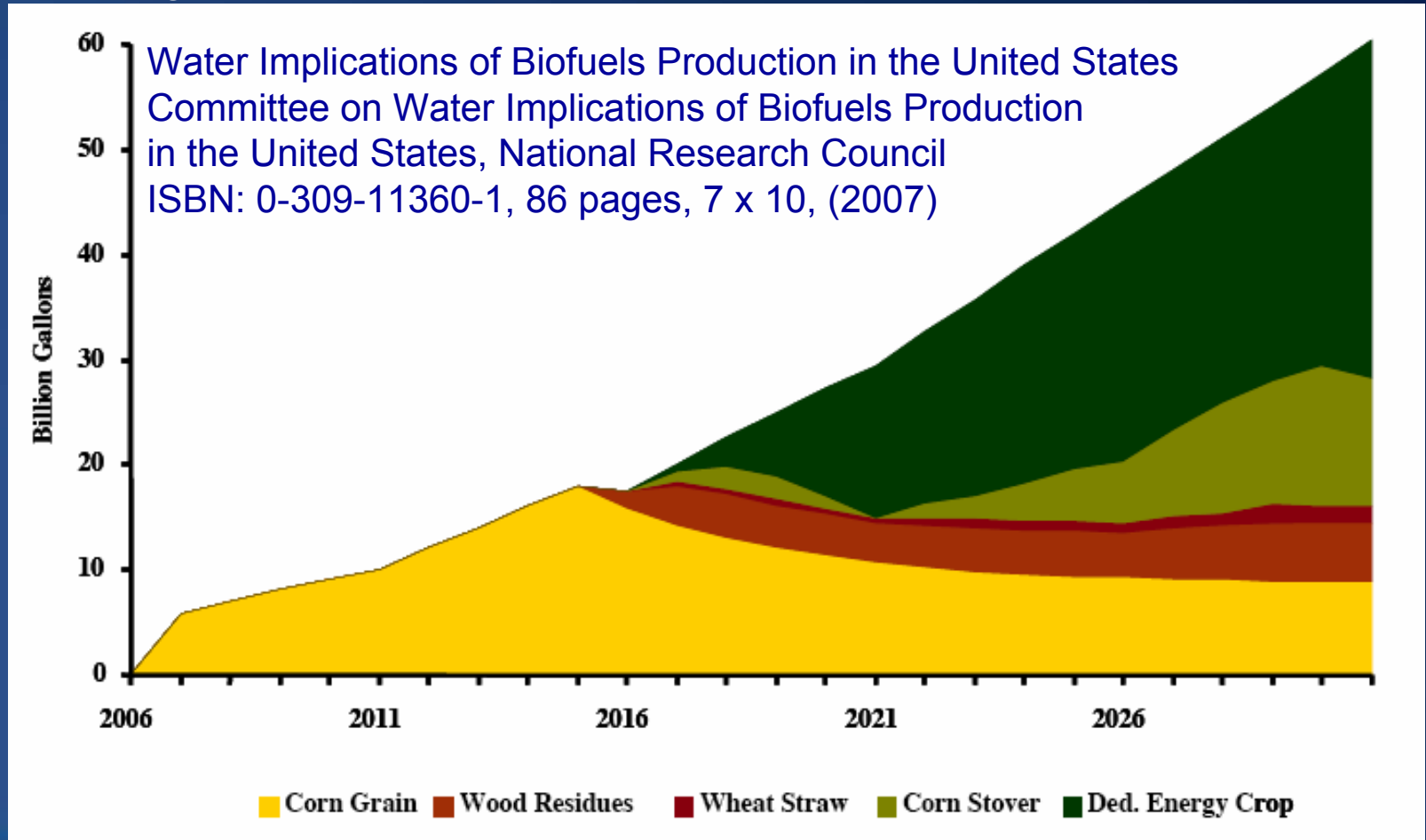


Trends in Water with New Energy



Trends in Biofuels

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

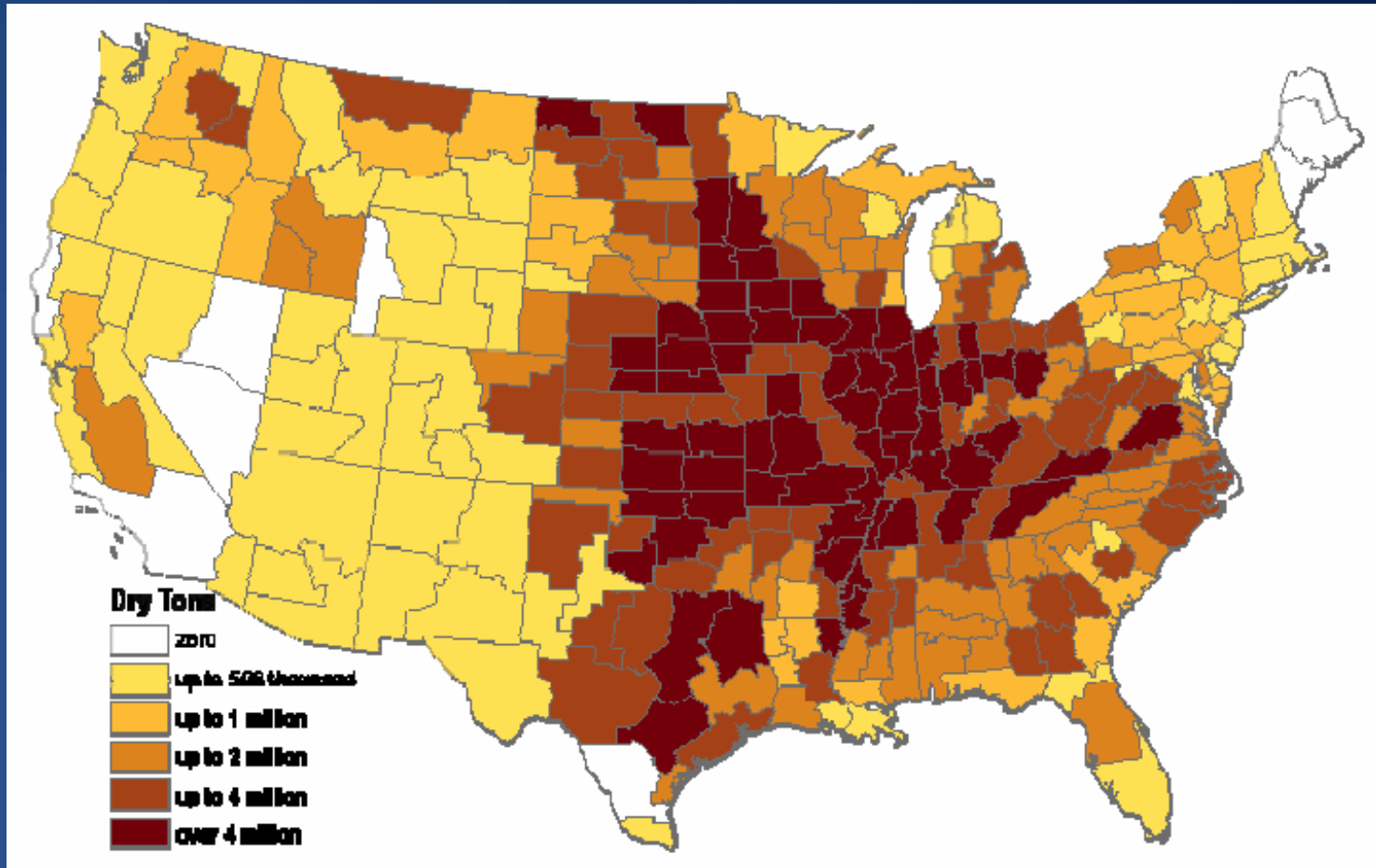


SOURCE: Reprinted, with permission, from D. Ugarte, University of Tennessee, written commun., July 12, 2007.



Trends in Biofuels

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

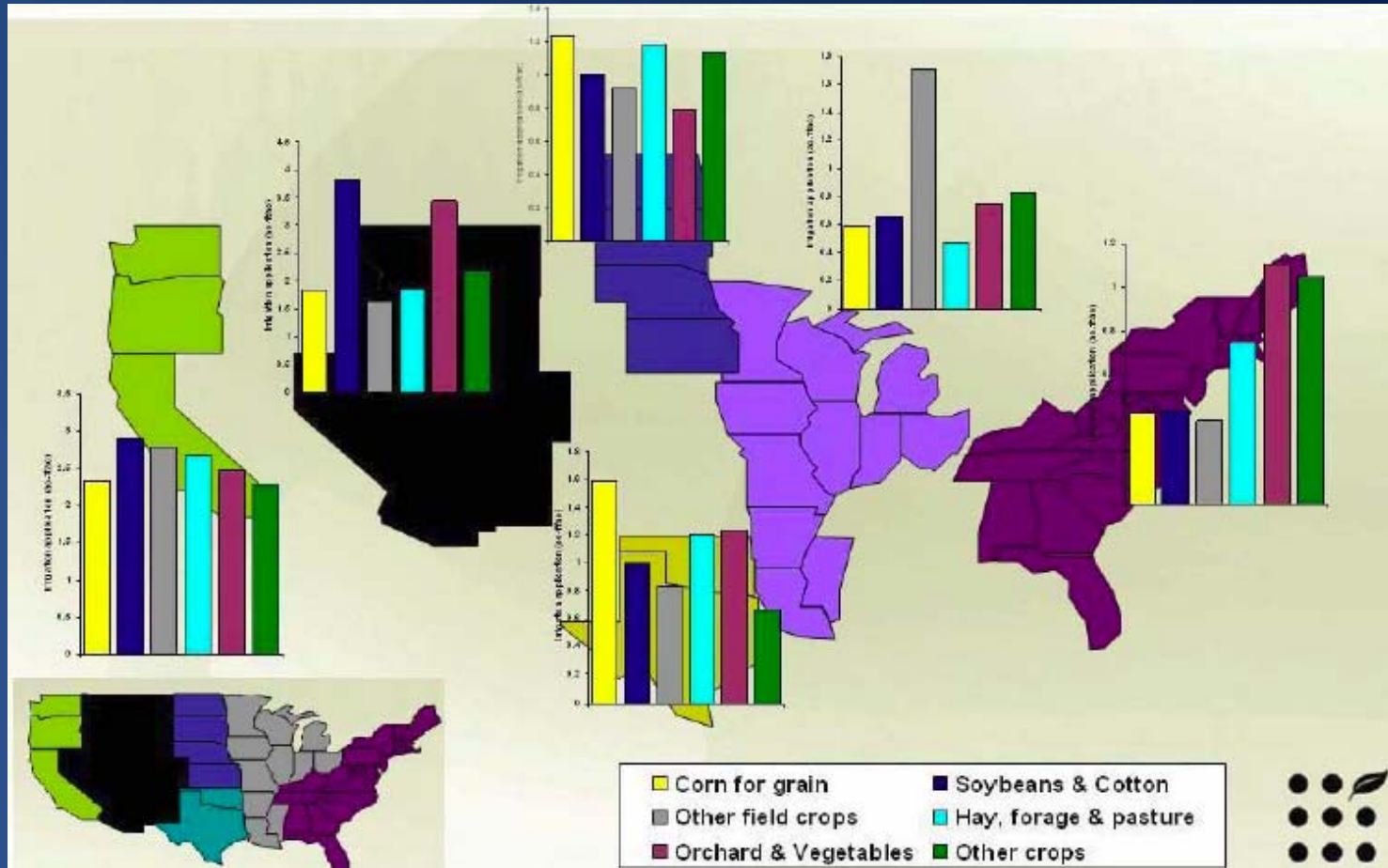


SOURCE: Reprinted, with permission, from D. Ugarte, University of Tennessee, written commun., July 12, 2007.



Trends in Crop Irrigation

Regional irrigation water application for various crops for six regions of the United States.

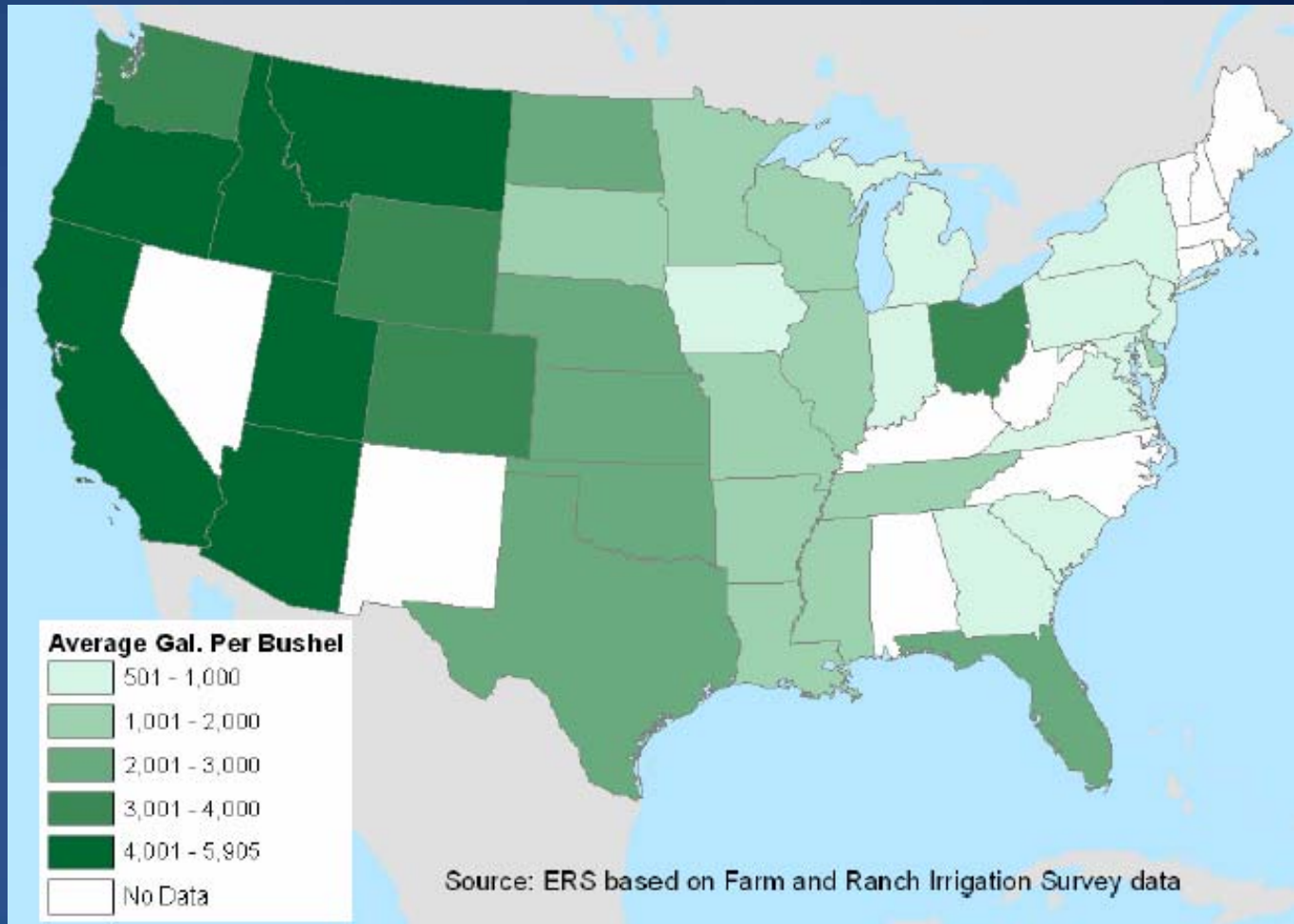


SOURCE: N. Gollehon, U.S. Department of Agriculture (USDA) Economic Research Service (ERS), written commun., July 12, 2007. Based on data from USDA Census of Agriculture.



Trends in Crop Irrigation

State-by-state water requirements in 2003 of irrigated corn (gal/bushel of irrigation water).

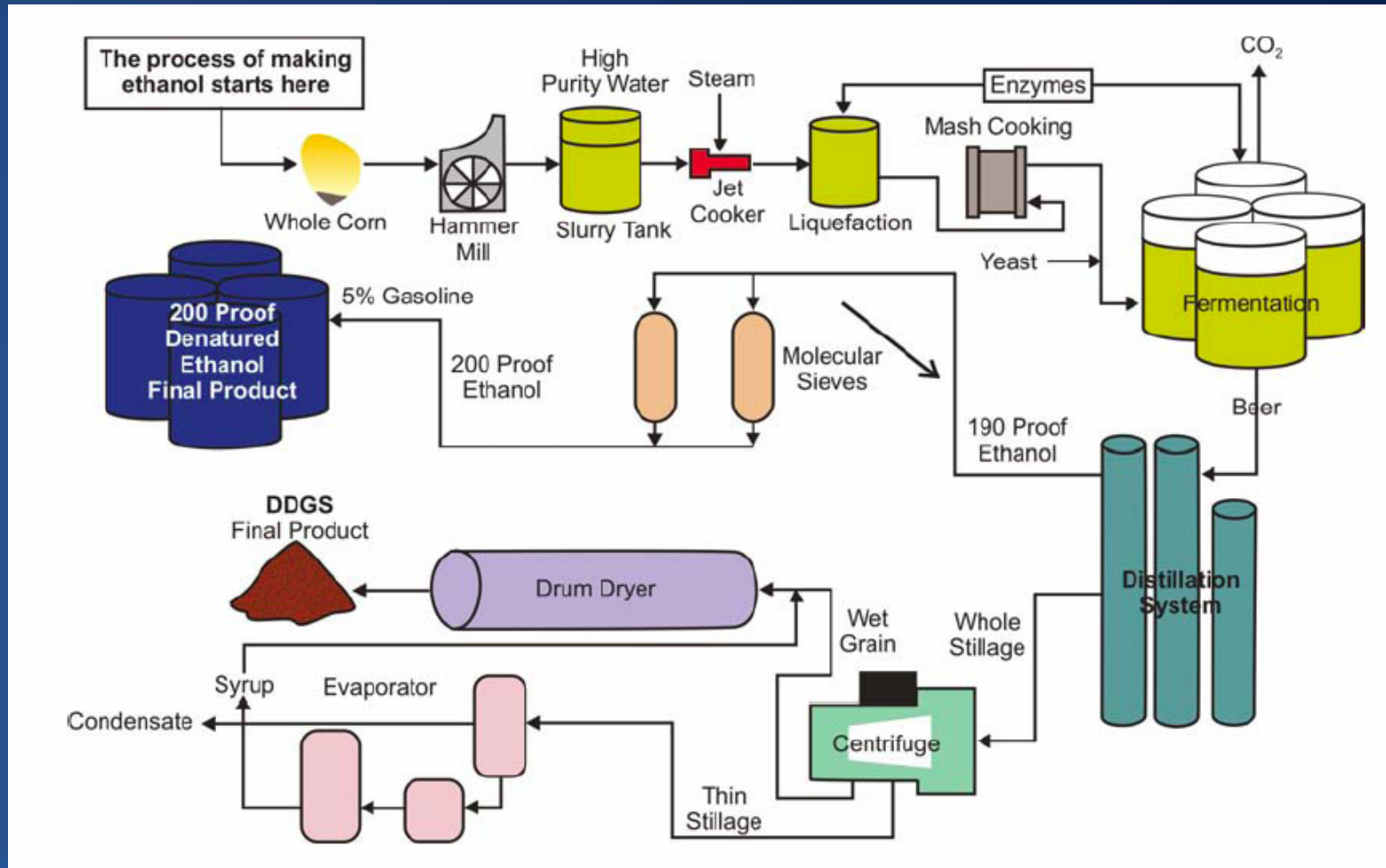


SOURCE: N. Gollehon, U.S. Department of Agriculture (USDA) Economic Research Service (ERS), written commun., July 12, 2007. Based on data from USDA Census of Agriculture.



Ethanol Production Facility

Water use throughout the processing of corn to ethanol.

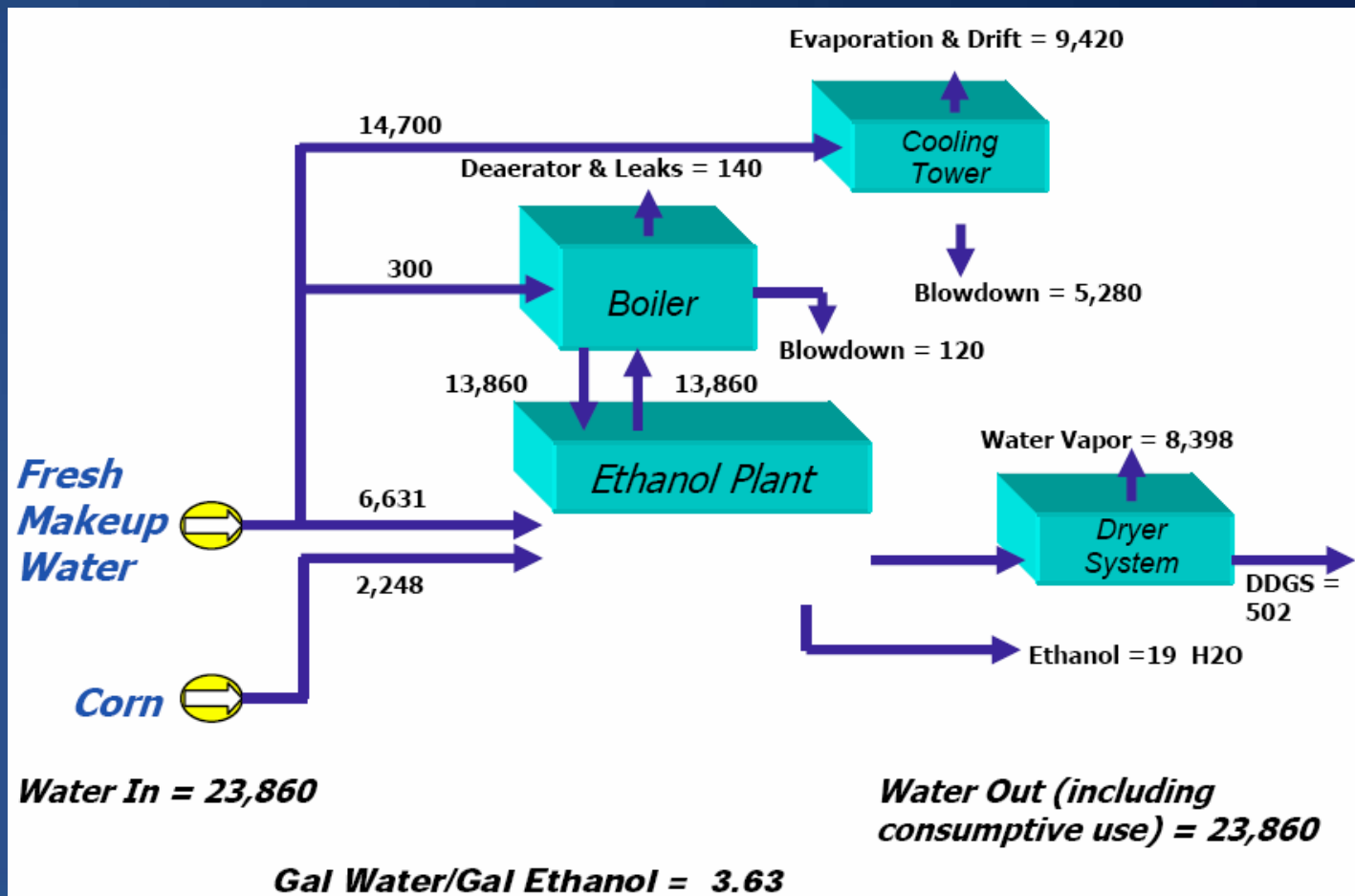


SOURCE: Parkin et al (2007).



Overall Water Balance

Water use for a 50 million/gallon year dry-mill ethanol processing plant.

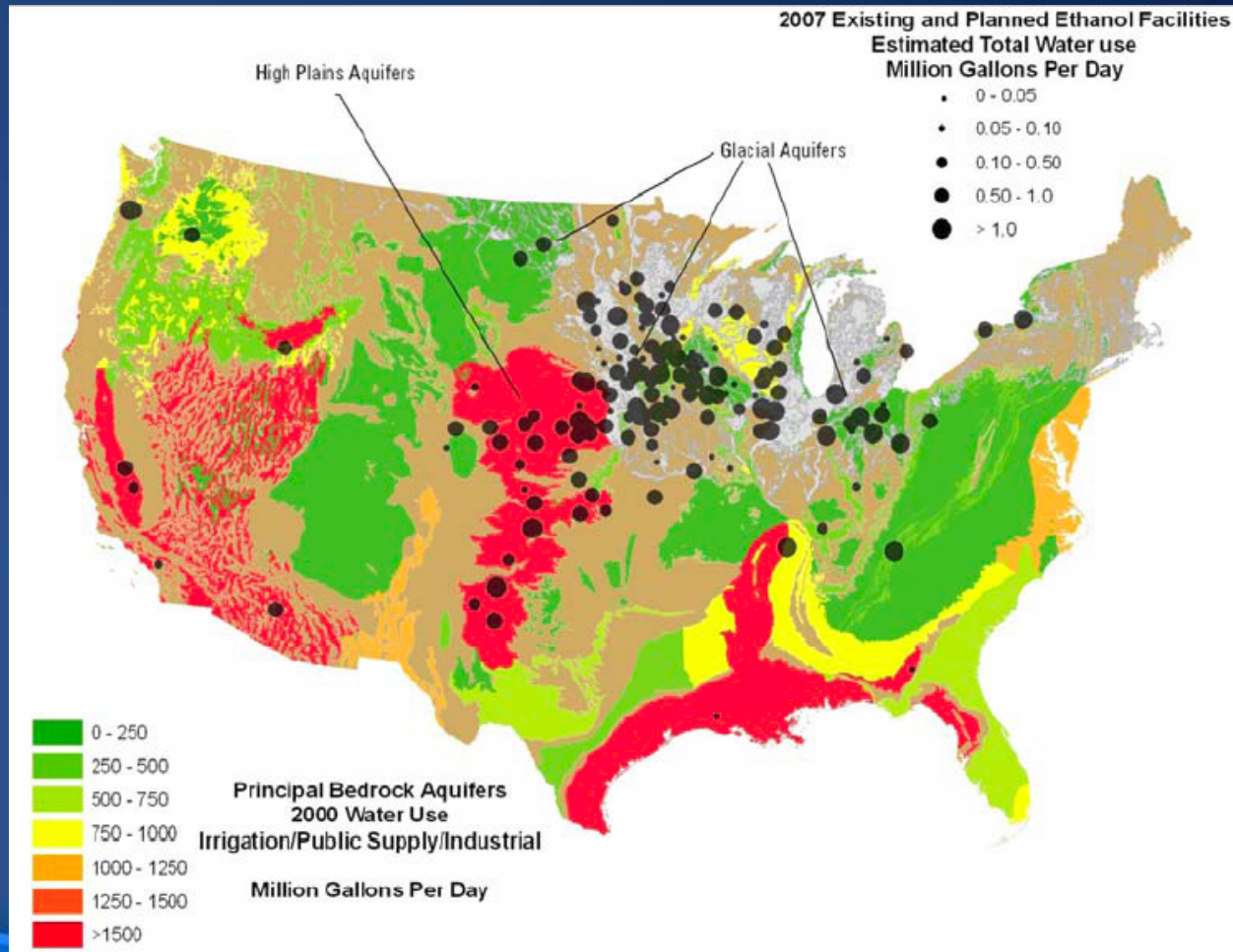


SOURCE: Courtesy of Delta-T Corp.



Ethanol Facility 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.



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

Water for Ethanol Refining: Source Matters!

Industrial Processing Water Use in Minnesota, 2004

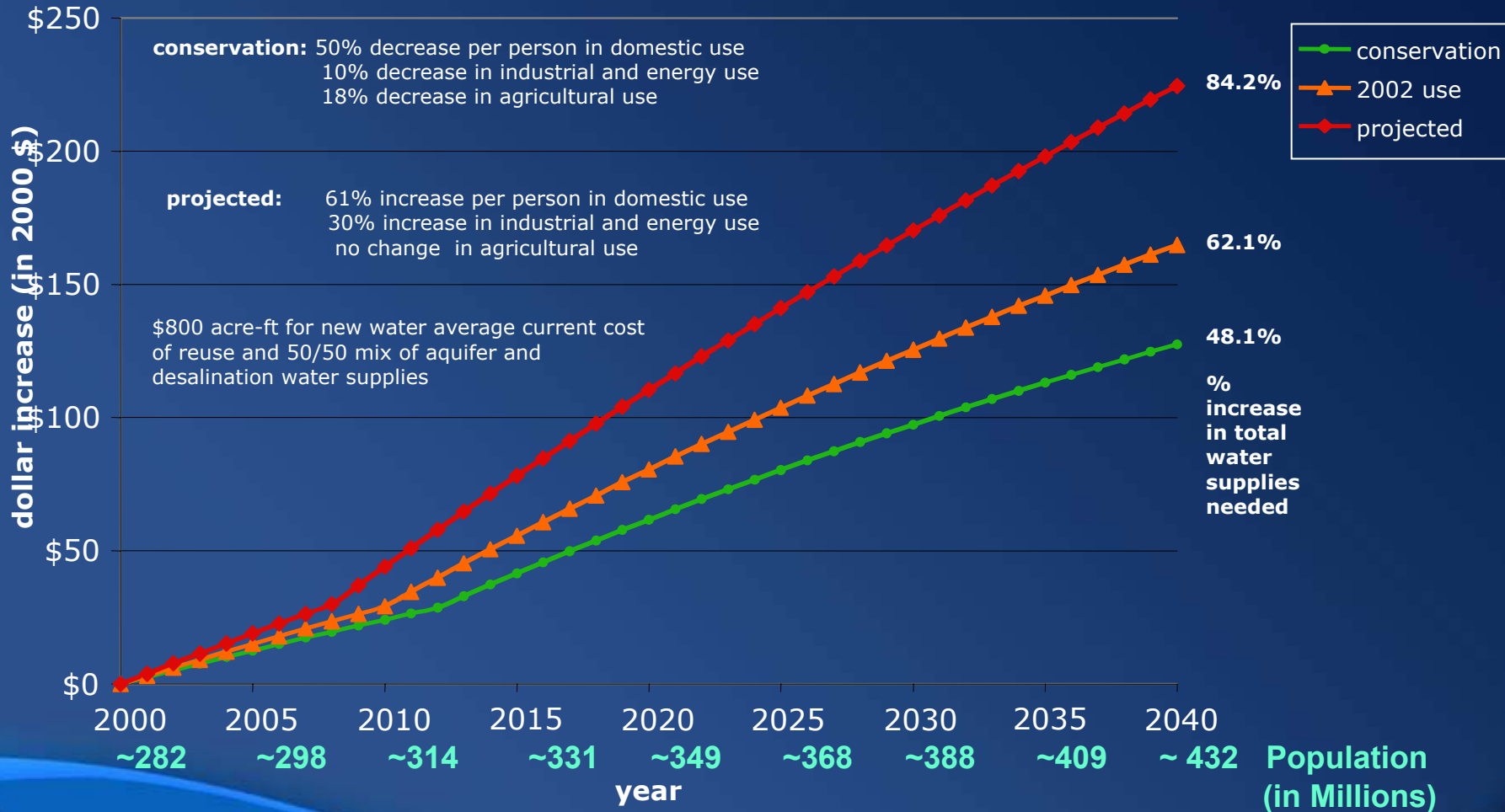
Category	Water Use, mgd		
	Ground Water	Surface Water	Total
Agricultural processing (food & livestock)	25.2	0.1	25.3
Pulp and paper processing	2.3	80.3	82.6
Mine processing (not sand & gravel washing)	0.5	296.5	297.0
Sand and gravel washing	3.8	7.5	11.3
Industrial process cooling once-through	5.8	0.5	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

20%
of
aquifer
draw

Source: MDNR Water Appropriations Permit Program, 2004

Water Cost Growth With Population

New water supplies at \$800 acre-ft with 1% population growth, and 10% aquifer depletion



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!



Opportunities

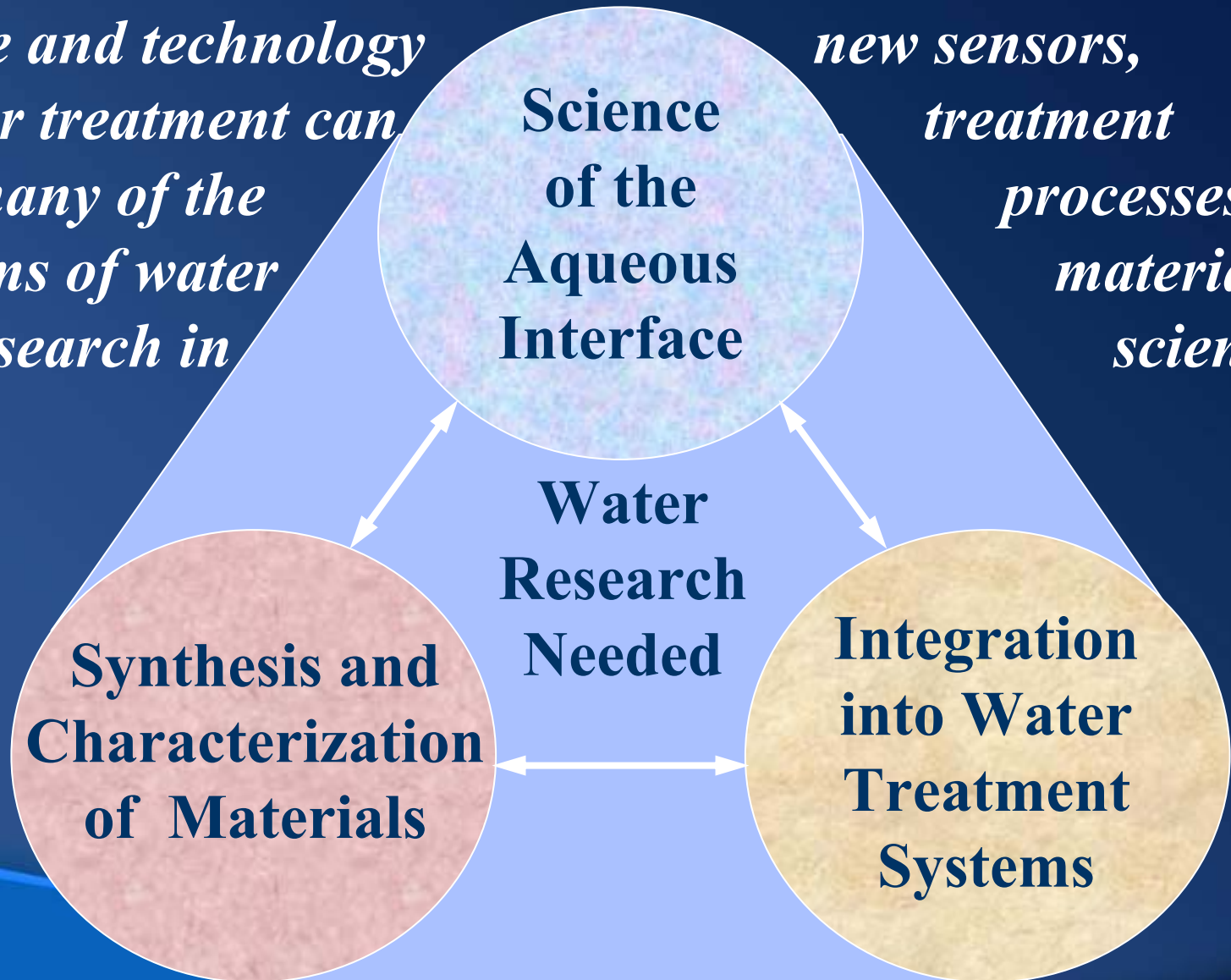
- 💧 Physically, we are far from the thermodynamic limits for separating unwanted species from water.
- 💧 New materials are being developed that exploit physics of the nanoscale at the water interface.
- 💧 Energy/water nexus just starting to be connected.



Science, Synthesis and Systems

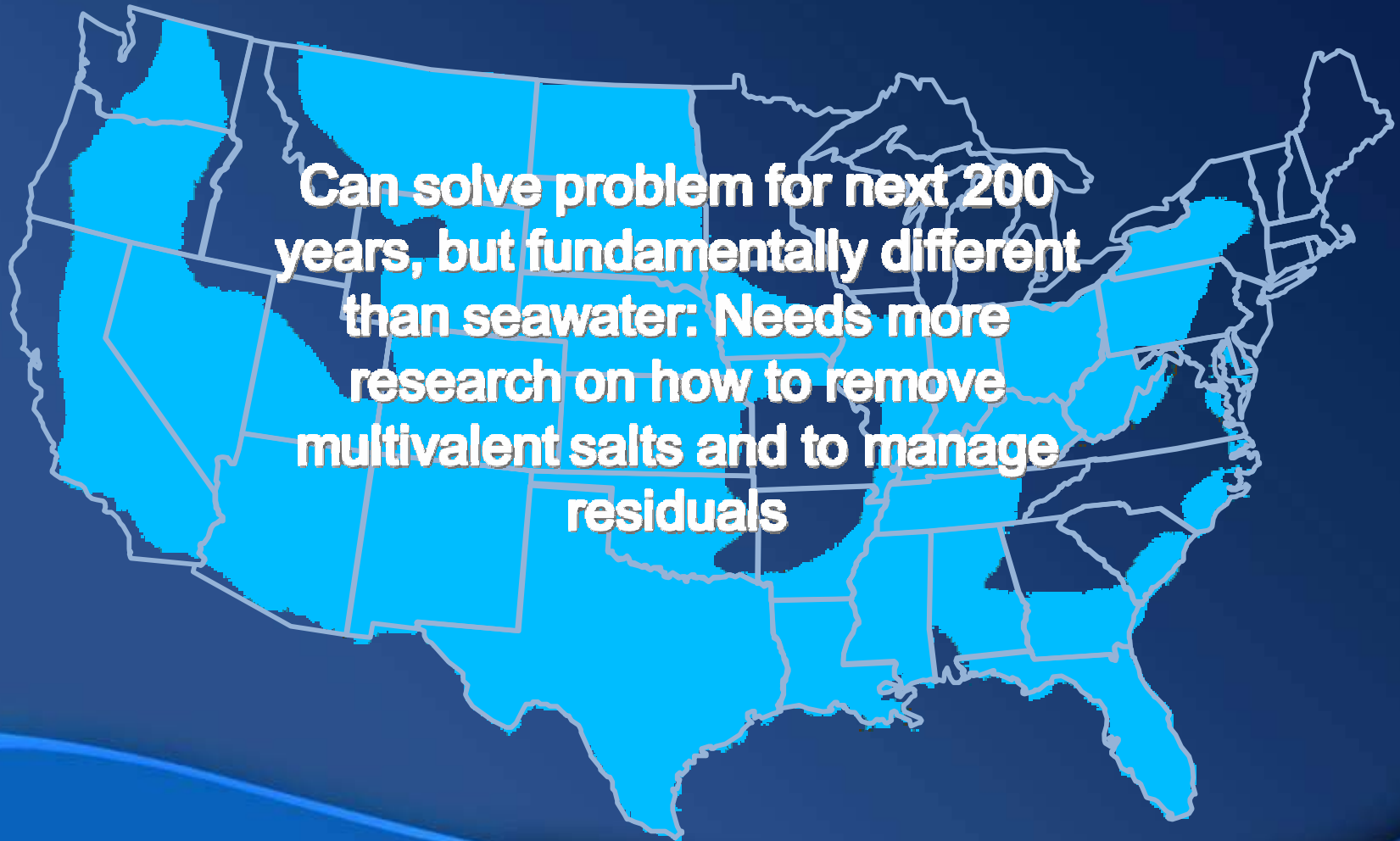
Science and technology of water treatment can solve many of the problems of water with research in

new sensors, treatment processes & material science.



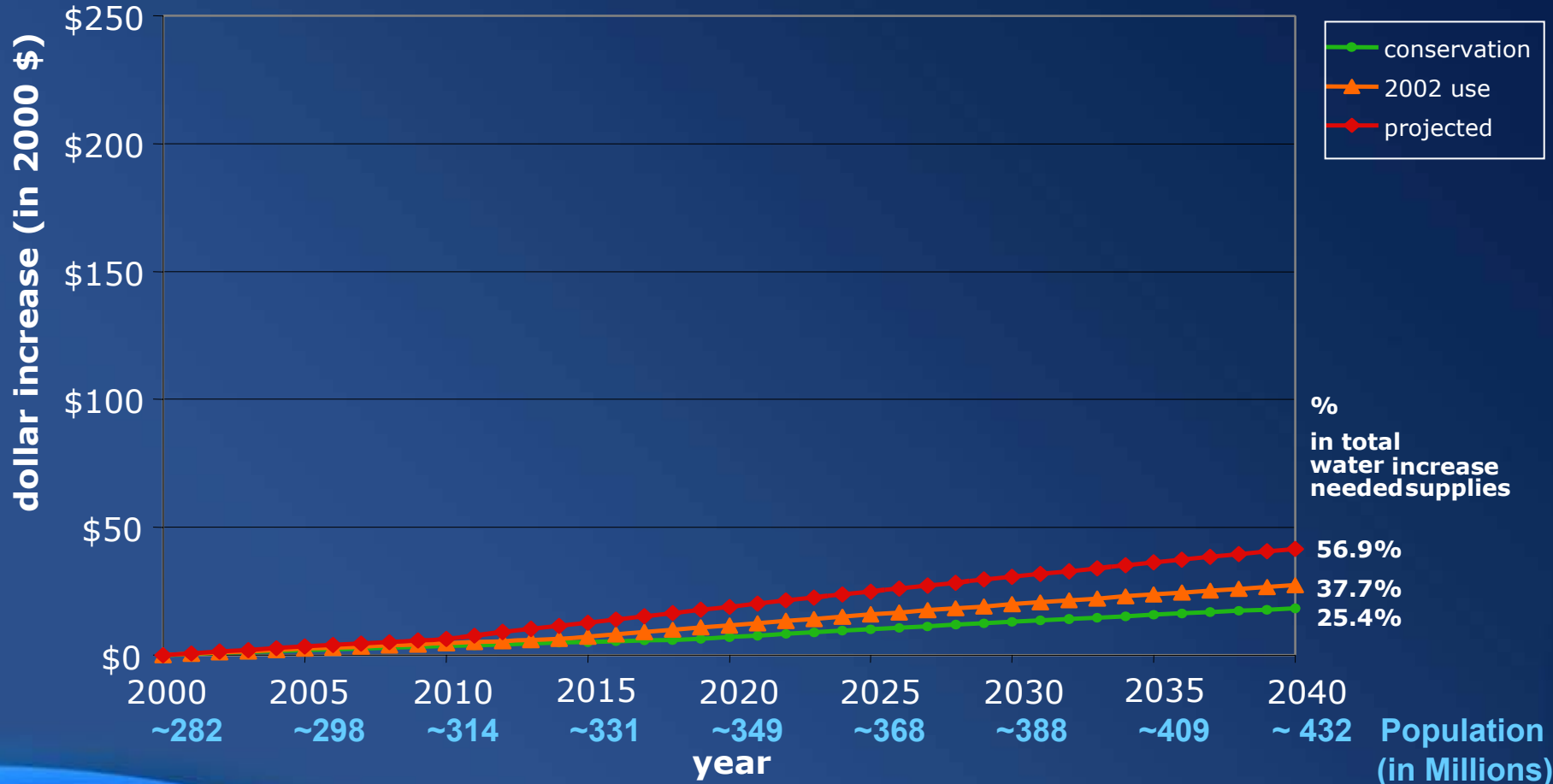
Growing the U.S. Water Supply

One solution is to utilize and reuse water from all sources such as saline aquifers shown above.



Water Cost Growth With Research

New water supplies at \$200 acre-ft with 1% population growth, and no aquifer depletion



Research Objectives

Organized in Interdisciplinary CAMPWS Teams (ICT's) to address three major objectives identified for water purification by **CAMPWS, NAS, Sandia, and EPA** :

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

ICT II. Remove contaminants from all types of water sources, to get the *“drop of poison out of an ocean of water.”*

ICT III. Disinfect water from current and potentially emerging pathogens without producing toxins, to *“beat chlorination.”*



Research Being Worked On By *WaterCAMPWS*

Selective sensing & adsorption of Pb, Hg, etc.

SFVS & new probes of material response

Membrane Bioreactors for wastewater reuse

Catalytic oxidation of micropollutants

Catalytic reduction of nitrates and other inorganic pollutants

Fouling studies and mitigation

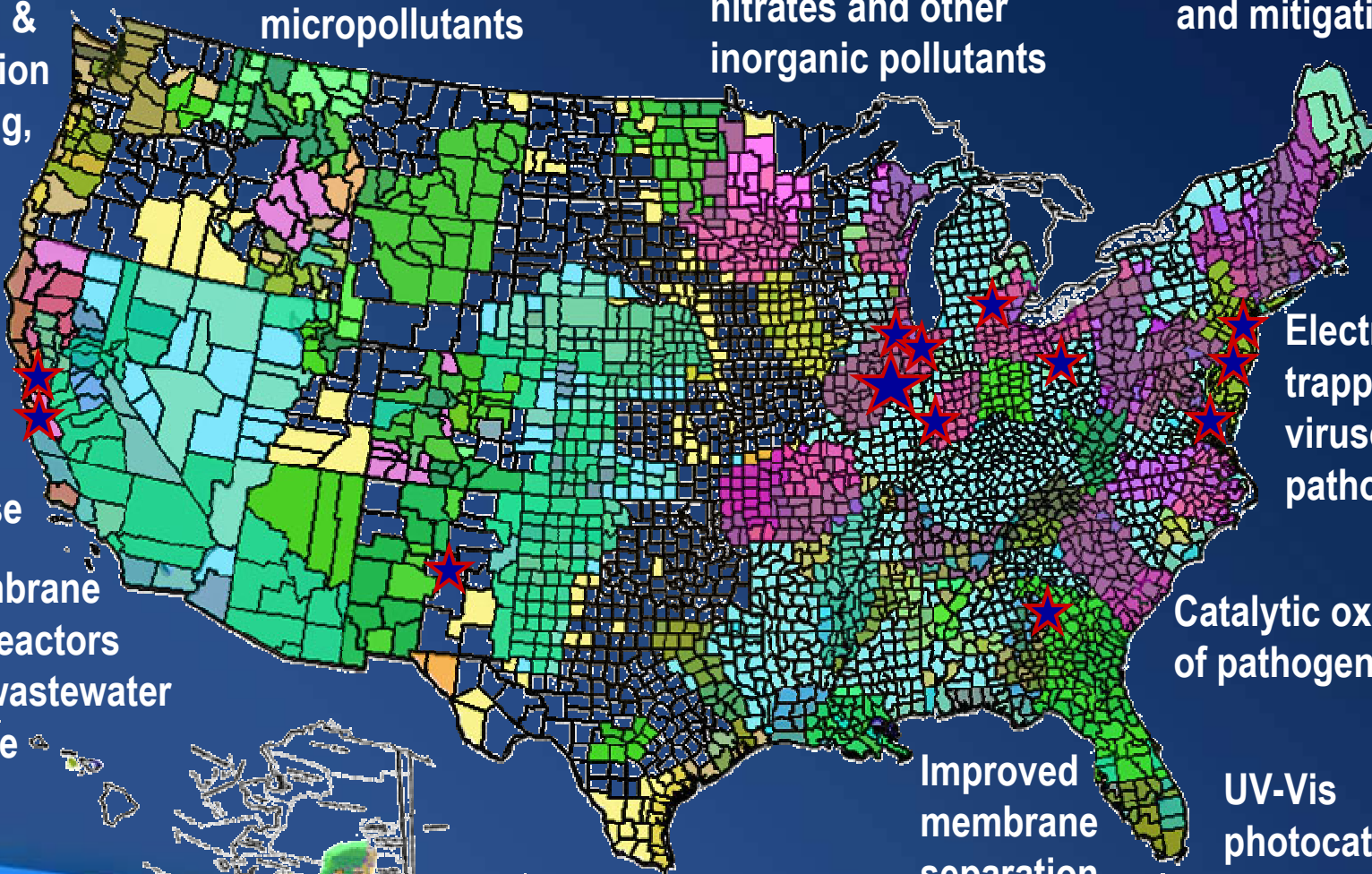
Electrostatic trapping of viruses and pathogens

Catalytic oxidation of pathogens

UV-Vis photocatalytic inactivation

Improved membrane separation processes

Freeze distillation to minimize residuals



Molecular Gates – Drivers for Development

Molecular gates are a new micro-nanofluidic construct recently developed at UIUC (last 6 years) by Bohn, Shannon, and Sweedler, along with many colleagues (Drs. Cannon, Fa, Flachsbart, Kuo, Long, Swearington, Tulock, Prakash...).

- ***Nano-Chemical-Mechanical-Manufacturing Systems (Nano-CEMMS)***



- Development of a nanomanufacturing system that utilizes molecular gates to meter attoliters of reactants in huge arrays.

- ***Center for Advanced Materials for Purification of Water with Systems (The WaterCAMPWS)***



- Utilizes molecular gates to separate ions from water
- Detection of sub-ppb toxic substances in water



Fundamental Issues to Sense Trace Contaminates in Water

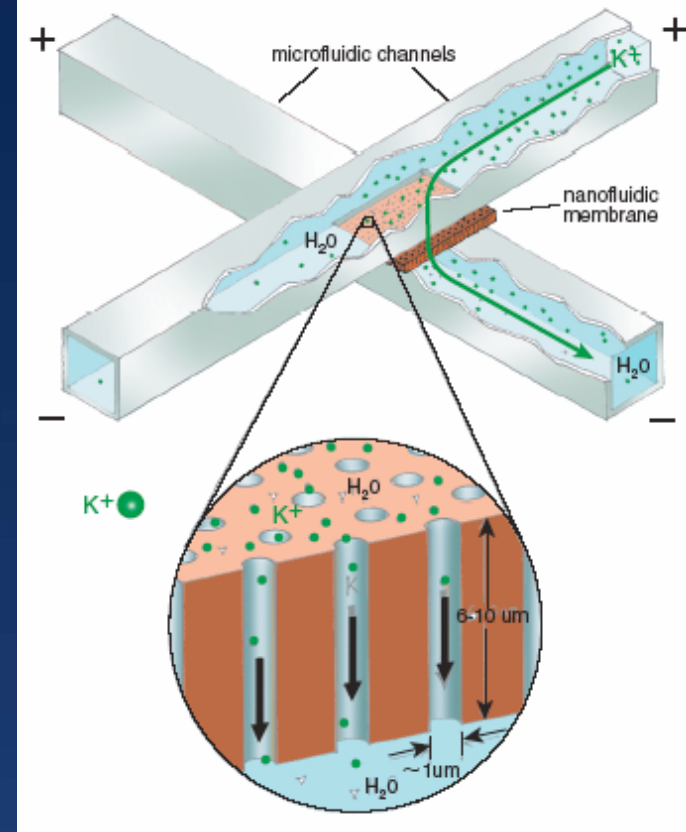
- ◆ ***Storage, Separating, Sensing, and Metering***
 - ◆ Sensing ultra-low concentrations of compounds: Needle in a trillion “haystacks” ($1:10^{12-20}$)
 - ◆ Meter out in ultra-low concentrations (down to attomolar)
- ◆ ***Transport of Molecules***
 - ◆ Due to composition, molecular structure and affinity, pH, ionic concentration, size, electrokinetic vs. pressure ...
- ◆ ***Delivery of Molecules***
 - ◆ Resolution, concentration, interfacing with systems, in huge arrays, and all the hard problems we are only beginning to look at...



What is a Molecular Gate?

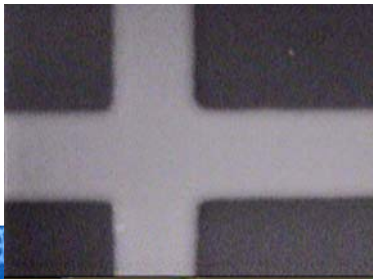
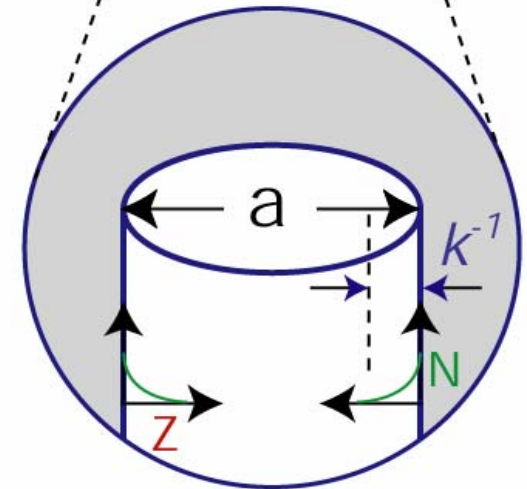
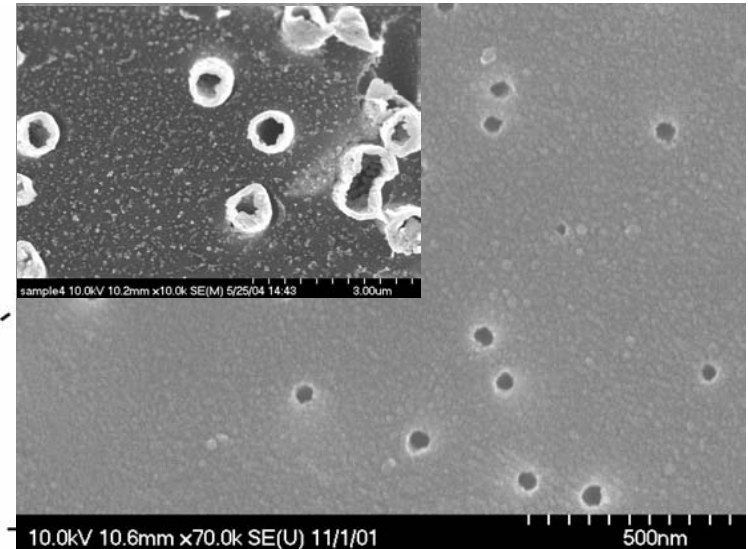
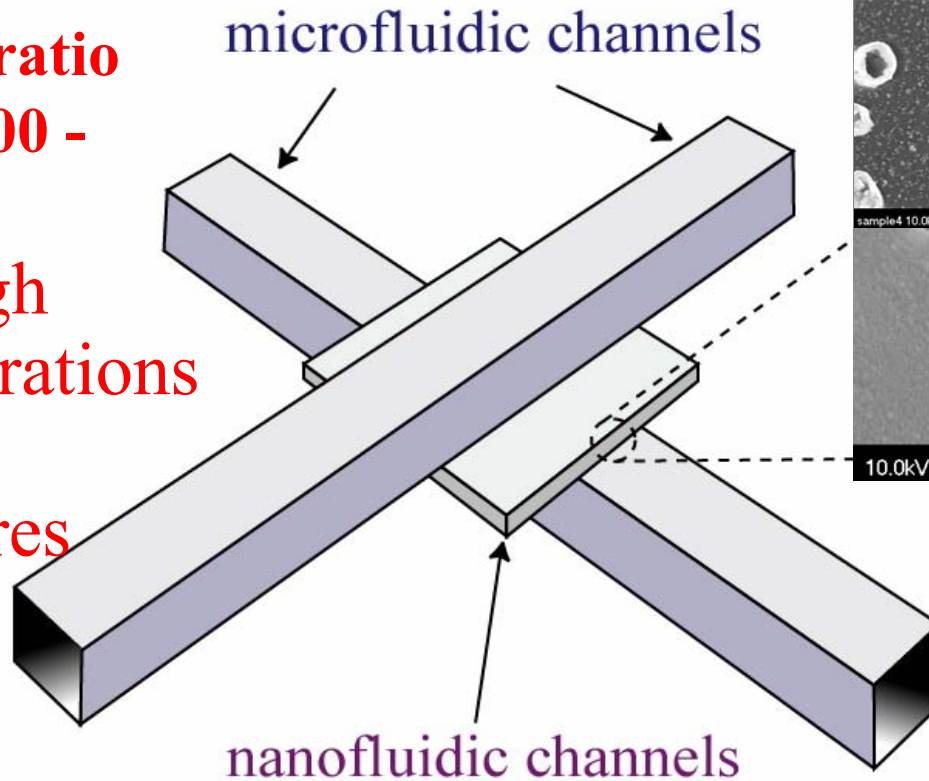
It is an *infinite aspect ratio*
micro-nanoscale construct that:

- Controls fluids like electronic devices control electrons
- Transport is proportional to applied bias (resistor)
Transport can be made to move in one direction (diode)
- Active control of fluid transport accomplishes digital transfer of fluids and solvated molecules
- Allows selective gating functions based on mass/size/affinity of molecules in fluid



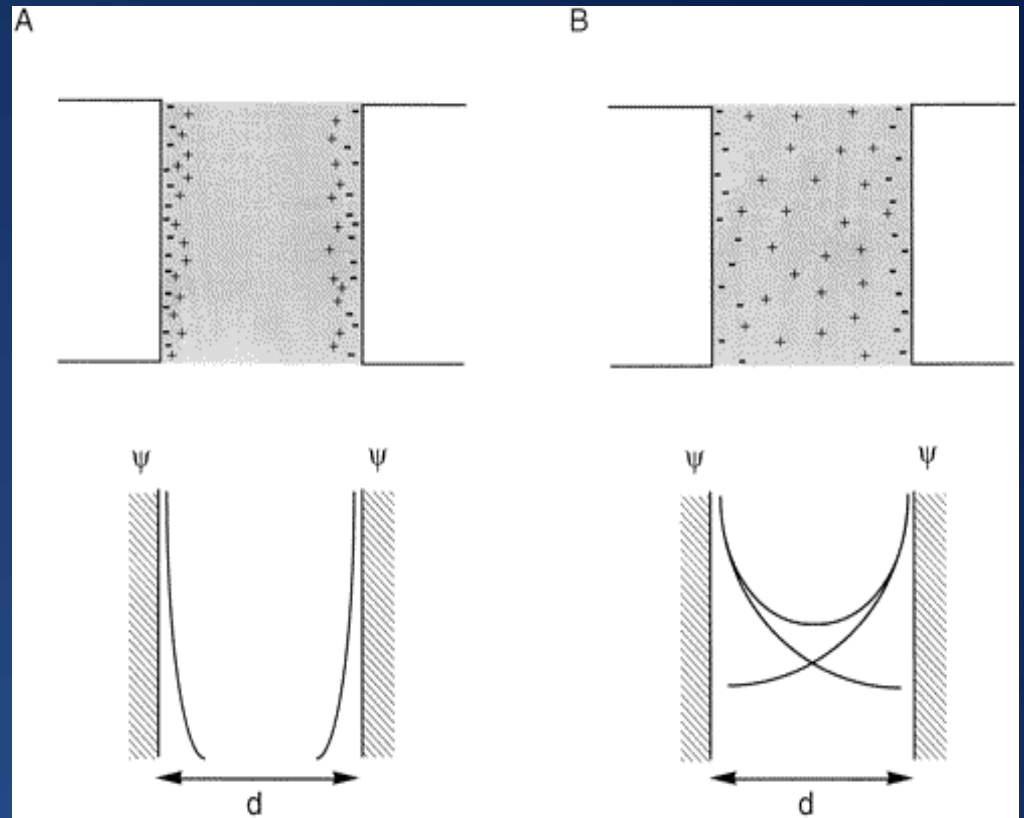
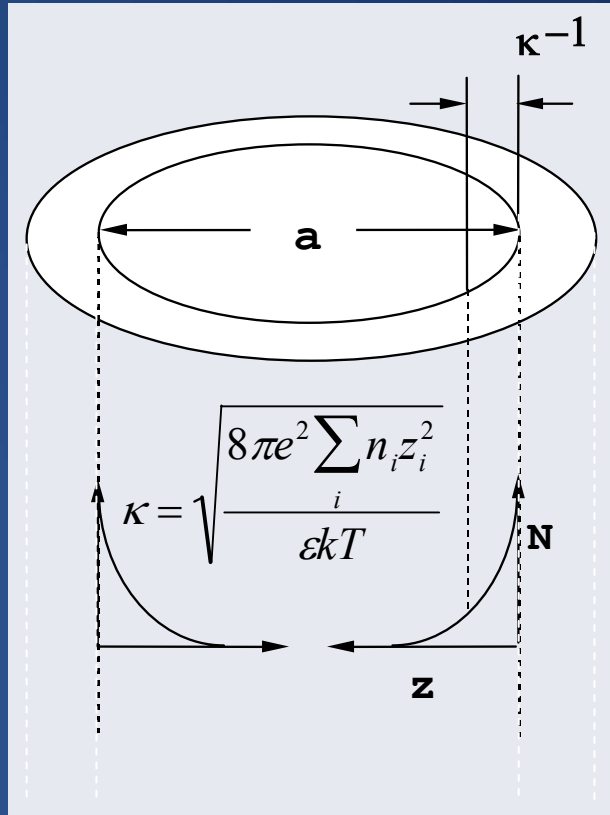
Micro/Nano Interconnect Creates a Gate

Pores with aspect ratio from 100 - 1000 very high concentrations within nanopores



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

When Will Nanofluidics Start to Dominate?



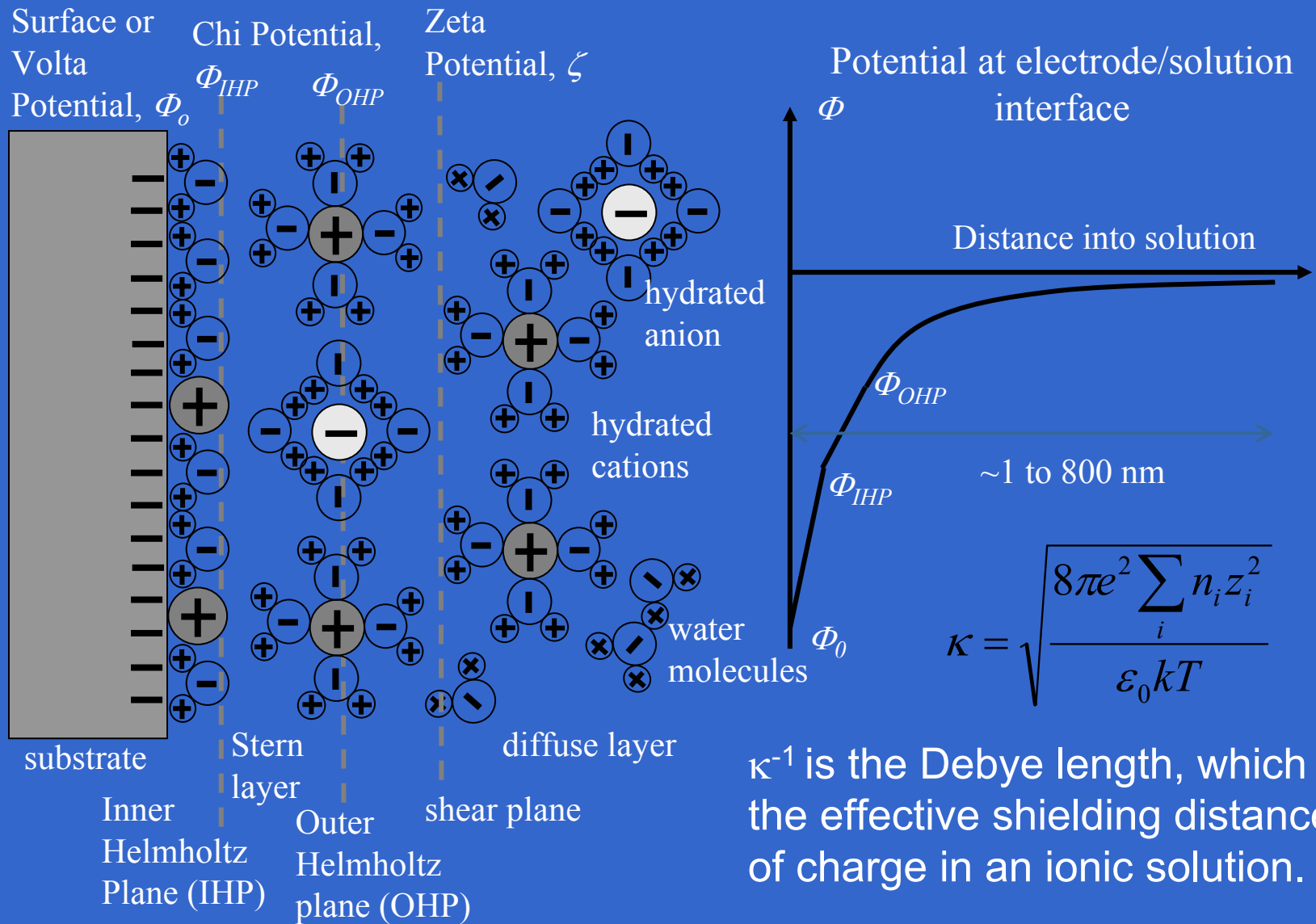
- Ionic strength adjusts κa
- At $\kappa a \ll 1$ electroosmotic flow dominates
- At $\kappa a \gg 1$ ion migration

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

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

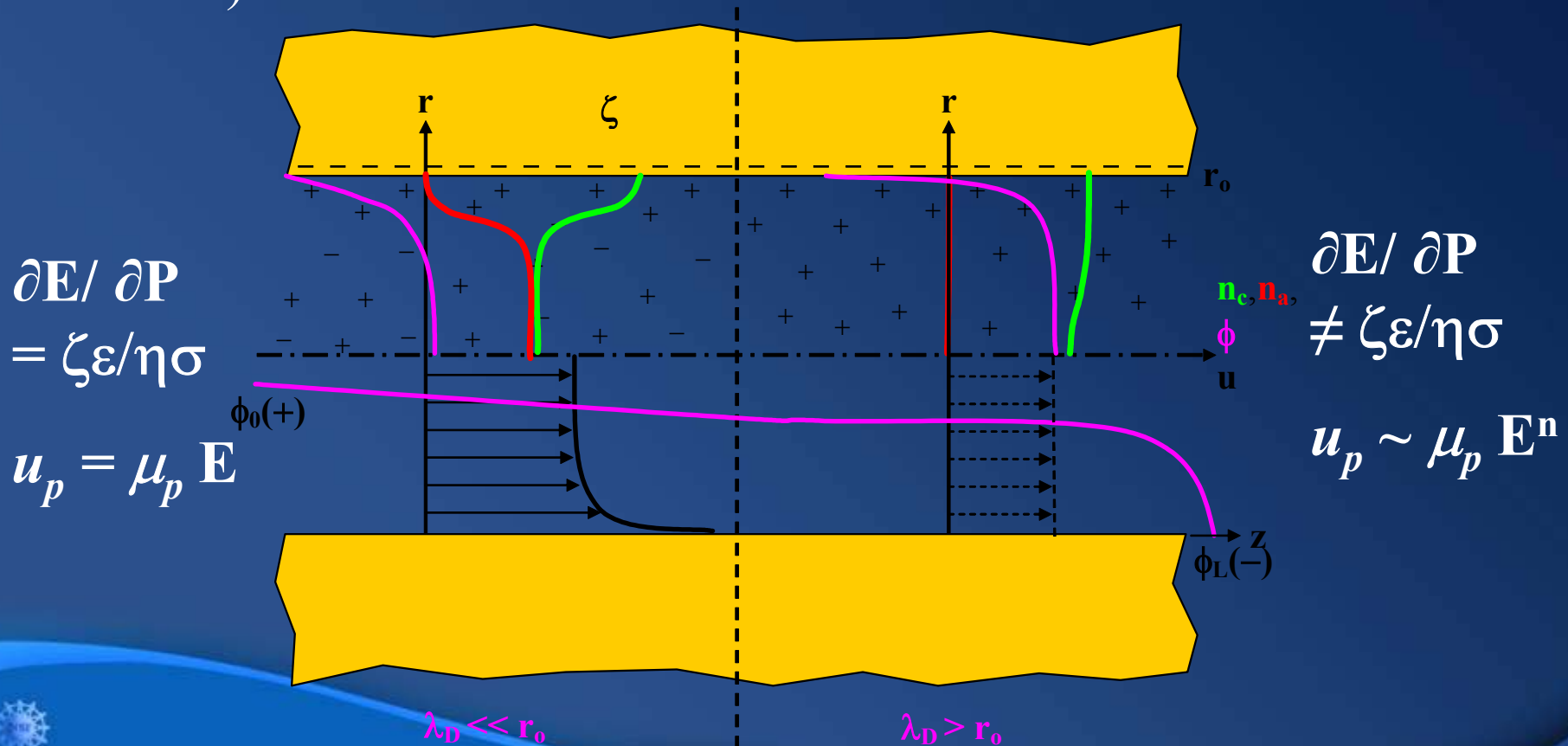


The Electric Double Layer in Fluid



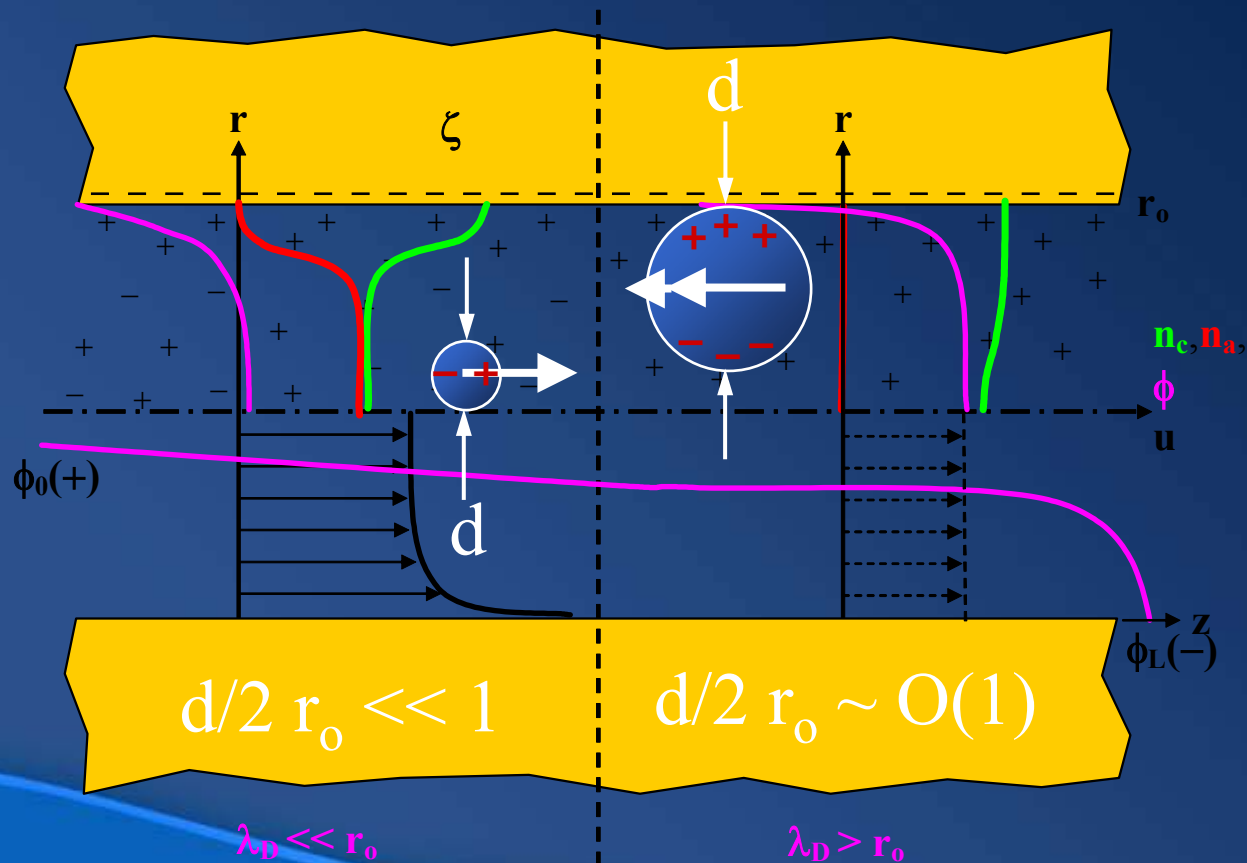
Effect of Debye Length, λ_D , on Profiles

- Non-linear transport at boundaries (ballistic and non-linear electrophoretic velocities: Helmholtz-Smoluchowski assumption violated)

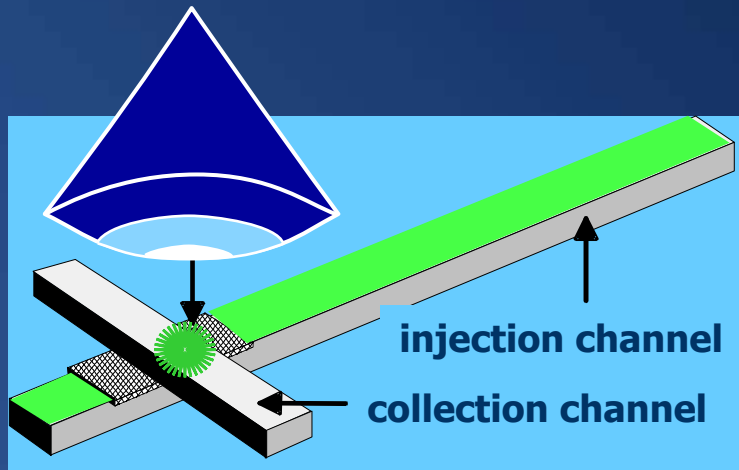


Effect of Debye Length, λ_D , on Profiles

- Spatial distribution of large molecules in channels favored at walls, leading to unusual molecular transport mechanisms.



Molecular Gate Operation

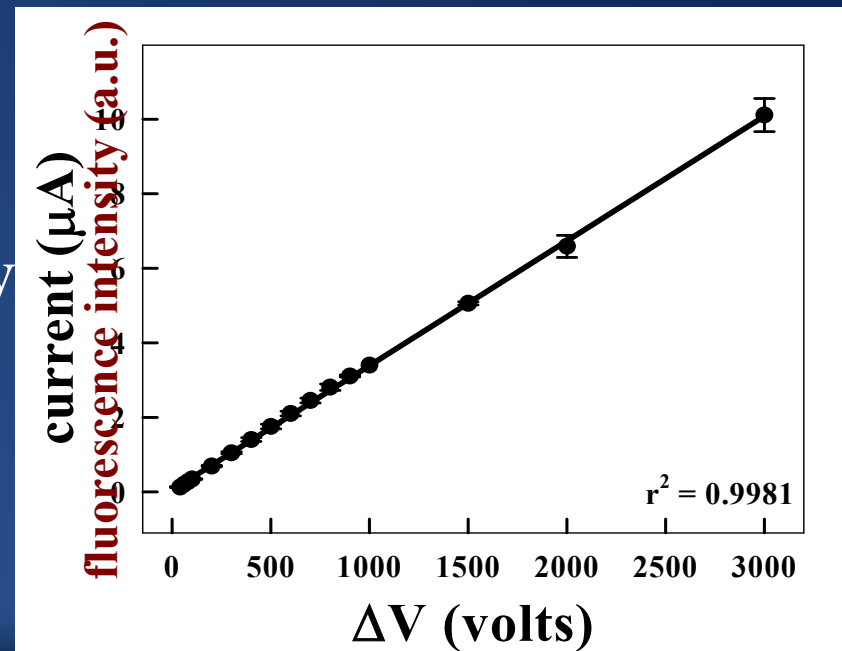
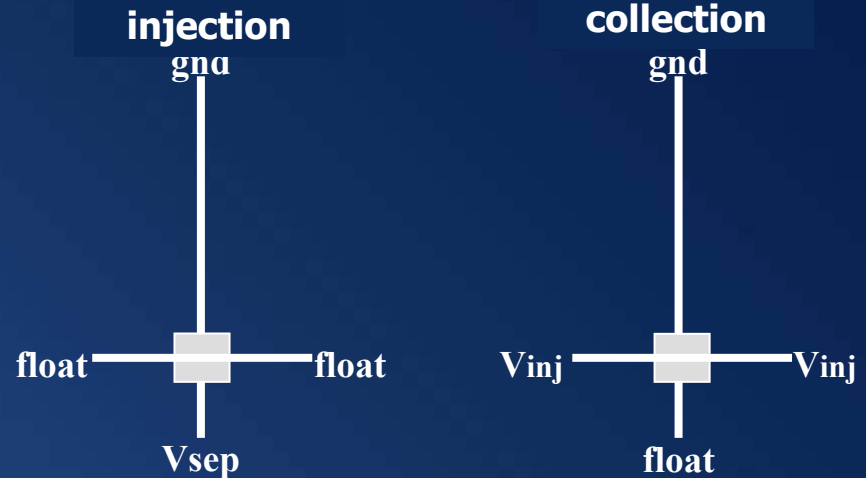


Pressure driven flow not suitable: Vanishingly small flows and pressure induced rupture occurs.

Electrokinetic flows extremely efficient: mm/s flows.

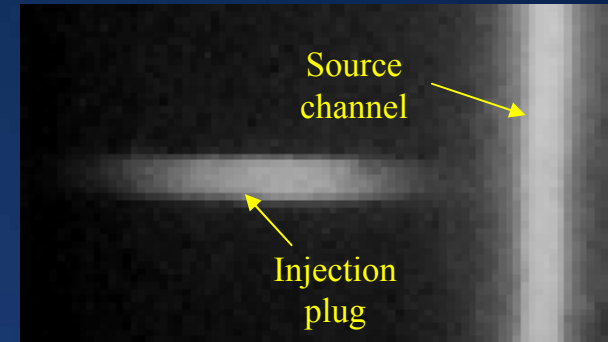
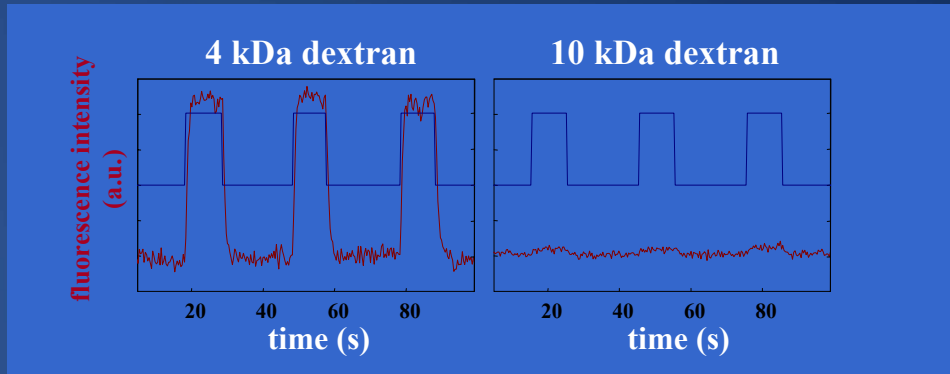
Operated by applying a voltage potential at the ends of the channels.

voltage pathways used for transport

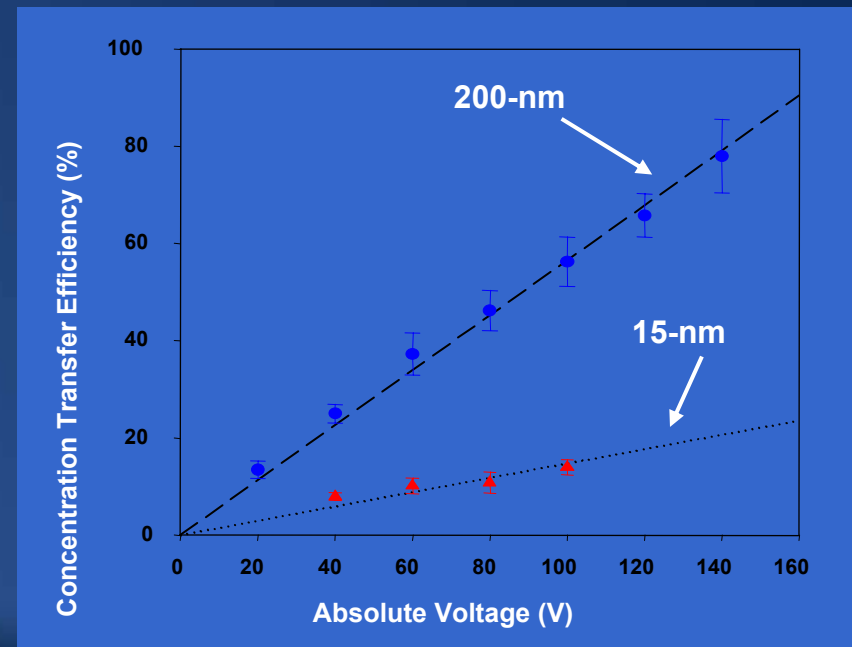


Control of Attomoles of Reactants

Active control of fluid transport accomplishes digital transfer of fluids and molecular species between microchannels.

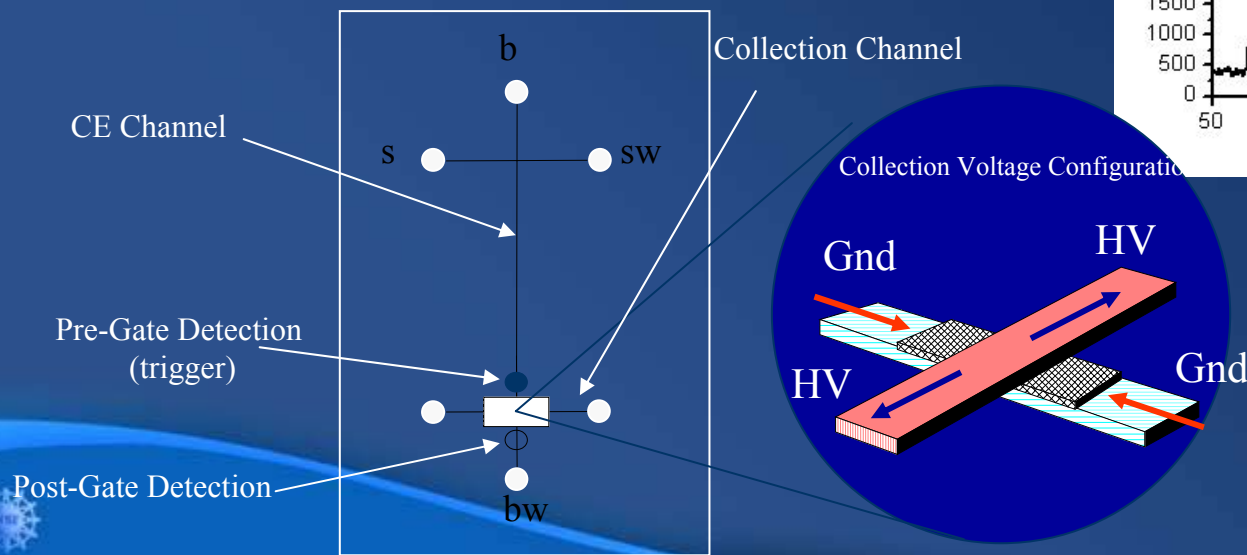
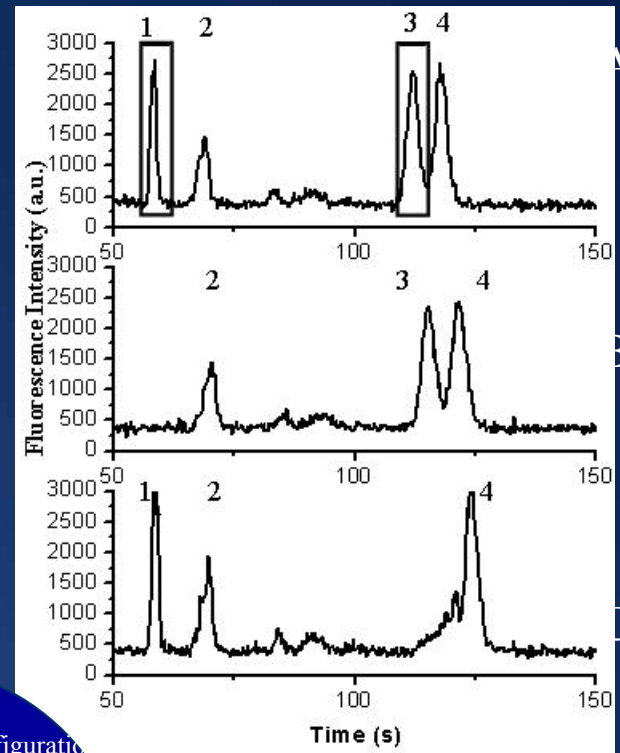


QuickTime™ and a Video decompressor are needed to see this picture.



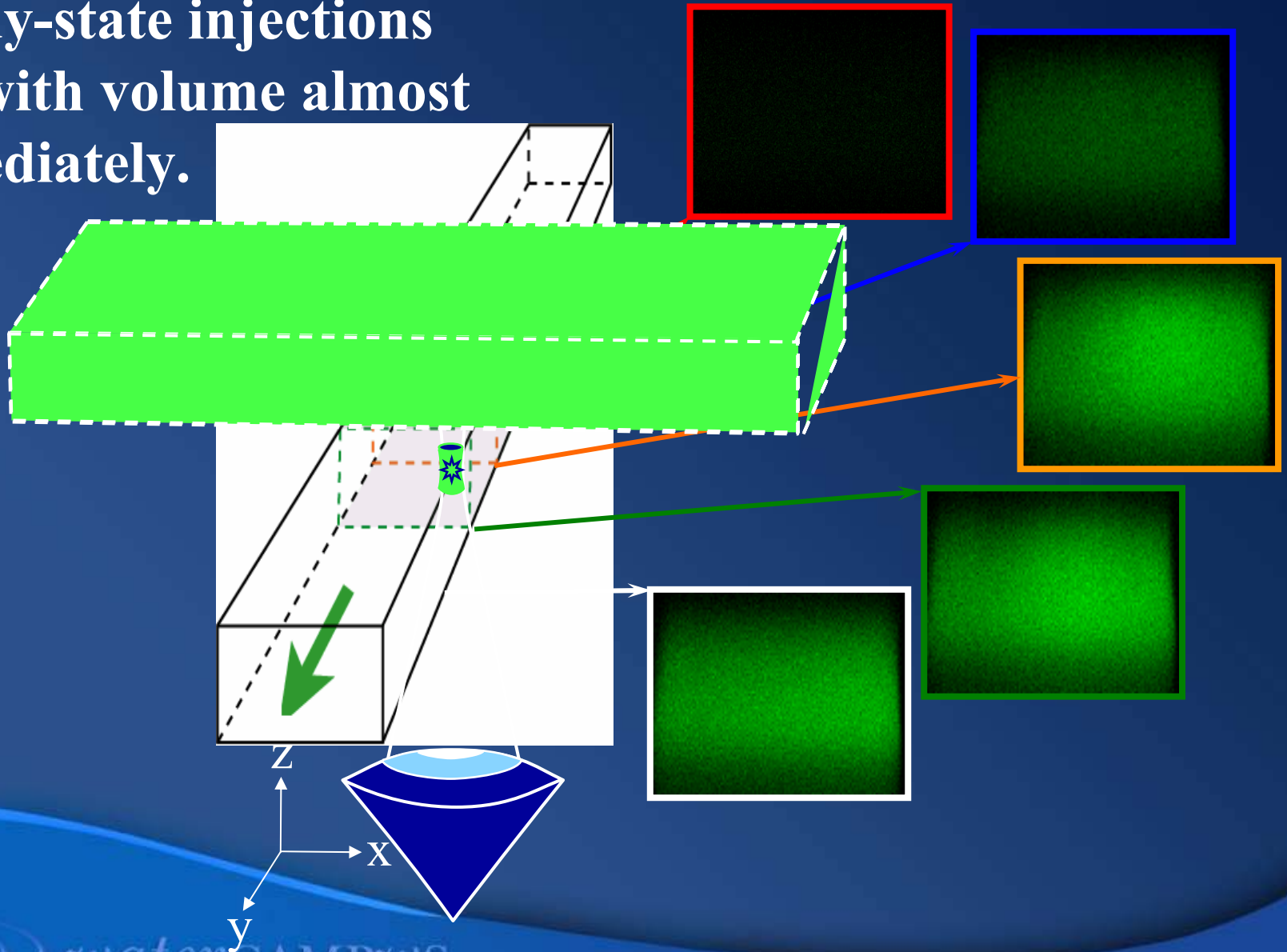
Capture of Analytes with Molecular Gates

Electrophoretic Separation and capture of FITC-Labeled Glutamate and Arginine in 50mM Borate Buffer ($E = 170 \text{ kV/cm}$).



Rapid Volumetric Mixing $Re \ll 1$ Laminar

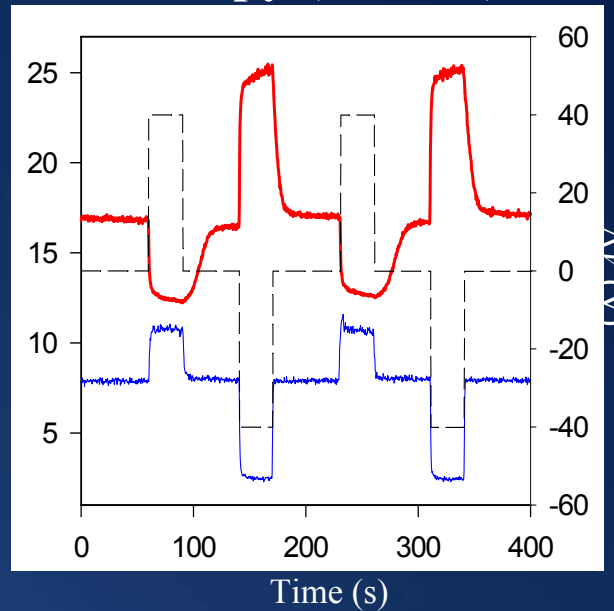
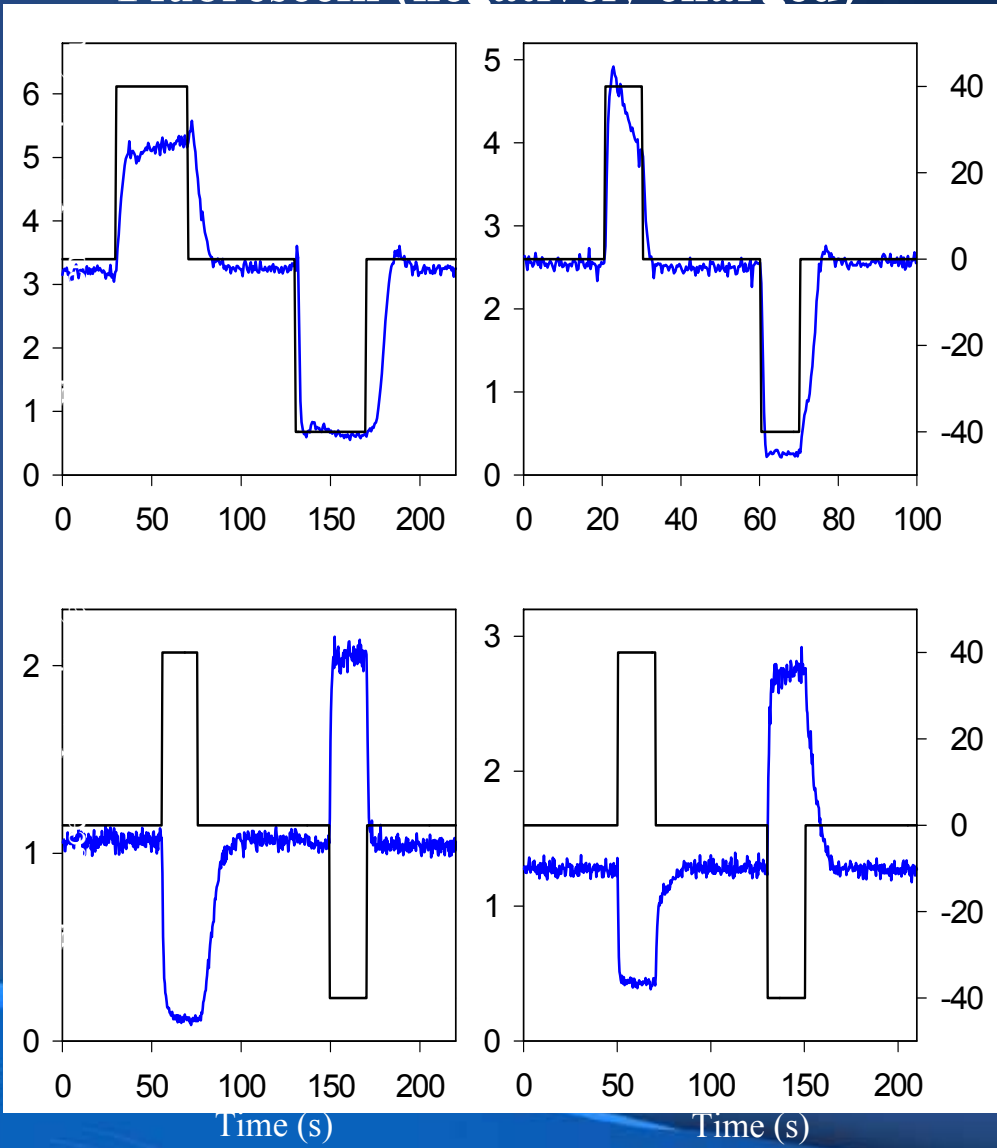
Steady-state injections
mix with volume almost
immediately.



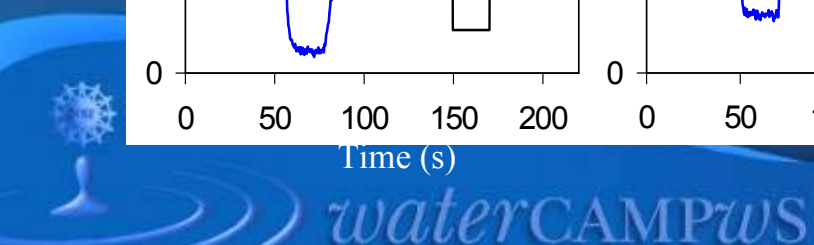
Effect of Pore Size on Transport Response

Fluorescein (negatively charged)

Bodipy (neutral)

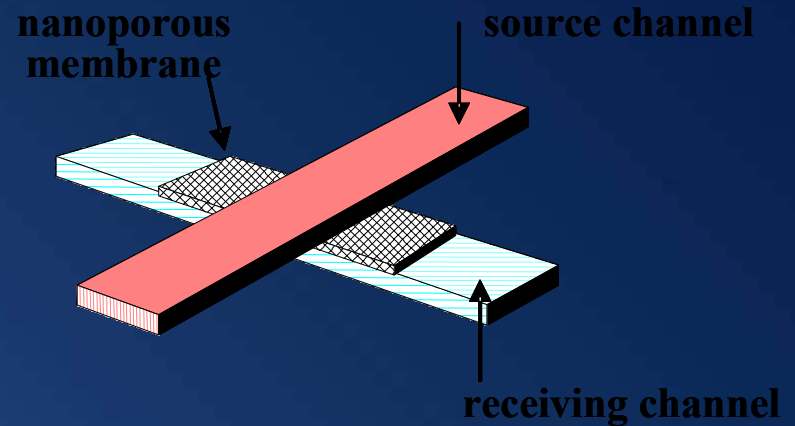
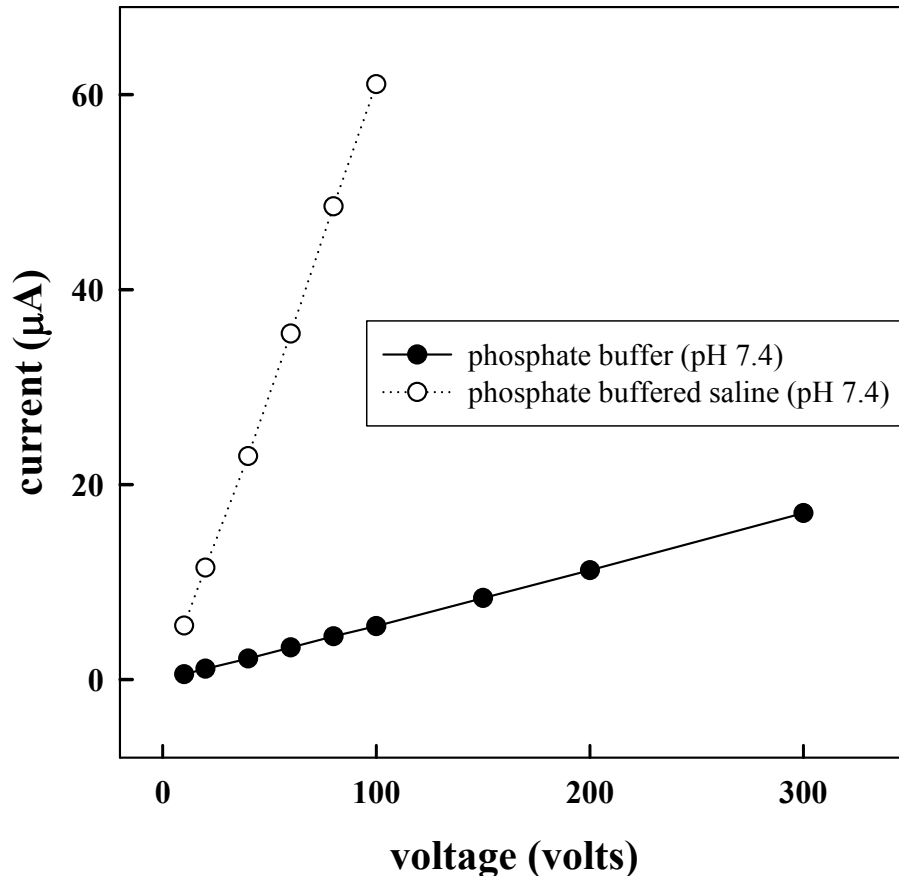


Flow direction for a given bias determined by wall charge, ionic strength, and pore diameter.



Gradients Across Channels

Injection of molecule from one solution to another.



Across 25 nm pores for two cases:

phosphate buffer (10 mM)

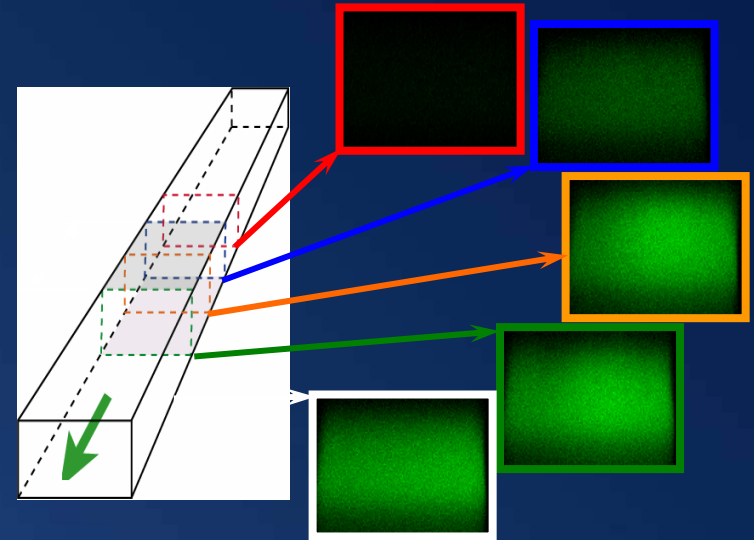
vs.

phosphate buffered saline (10 mM)

(138 mM NaCl; 2.7 mM KCl)

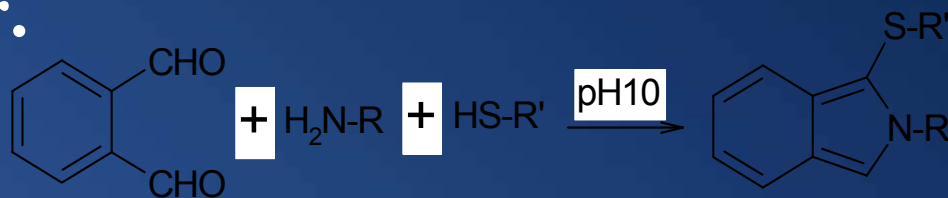
Challenges with Integrating Molecular Gates

**Molecules are not electrons:
Distinguishably different, and
behave differently for same
elements.**



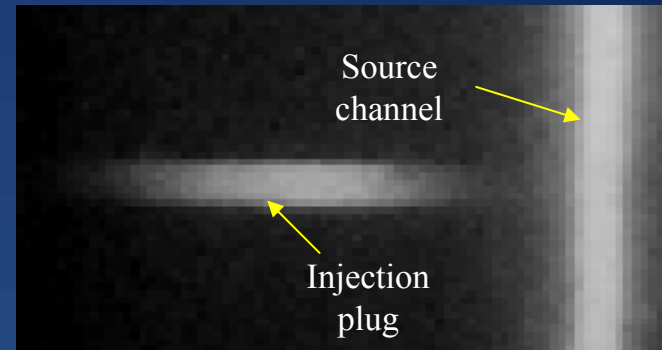
Challenges with Integrating Molecular Gates

Reactions: Change composition and behavior.

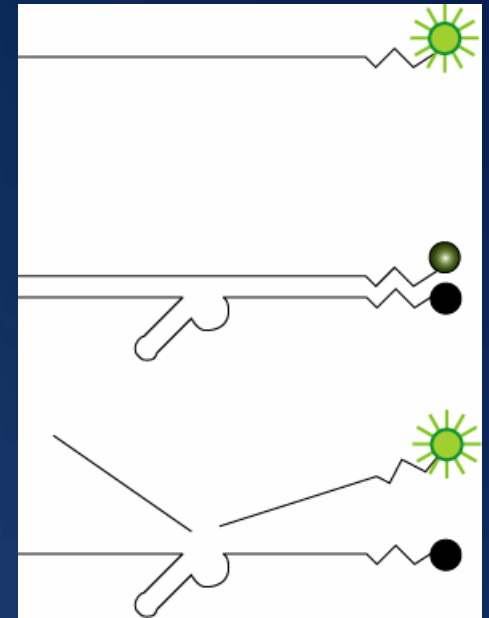


Challenges with Integrating Molecular Gates

Fluid Flow Strongly Coupled: Active control of fluid transport affected by previous interactions.



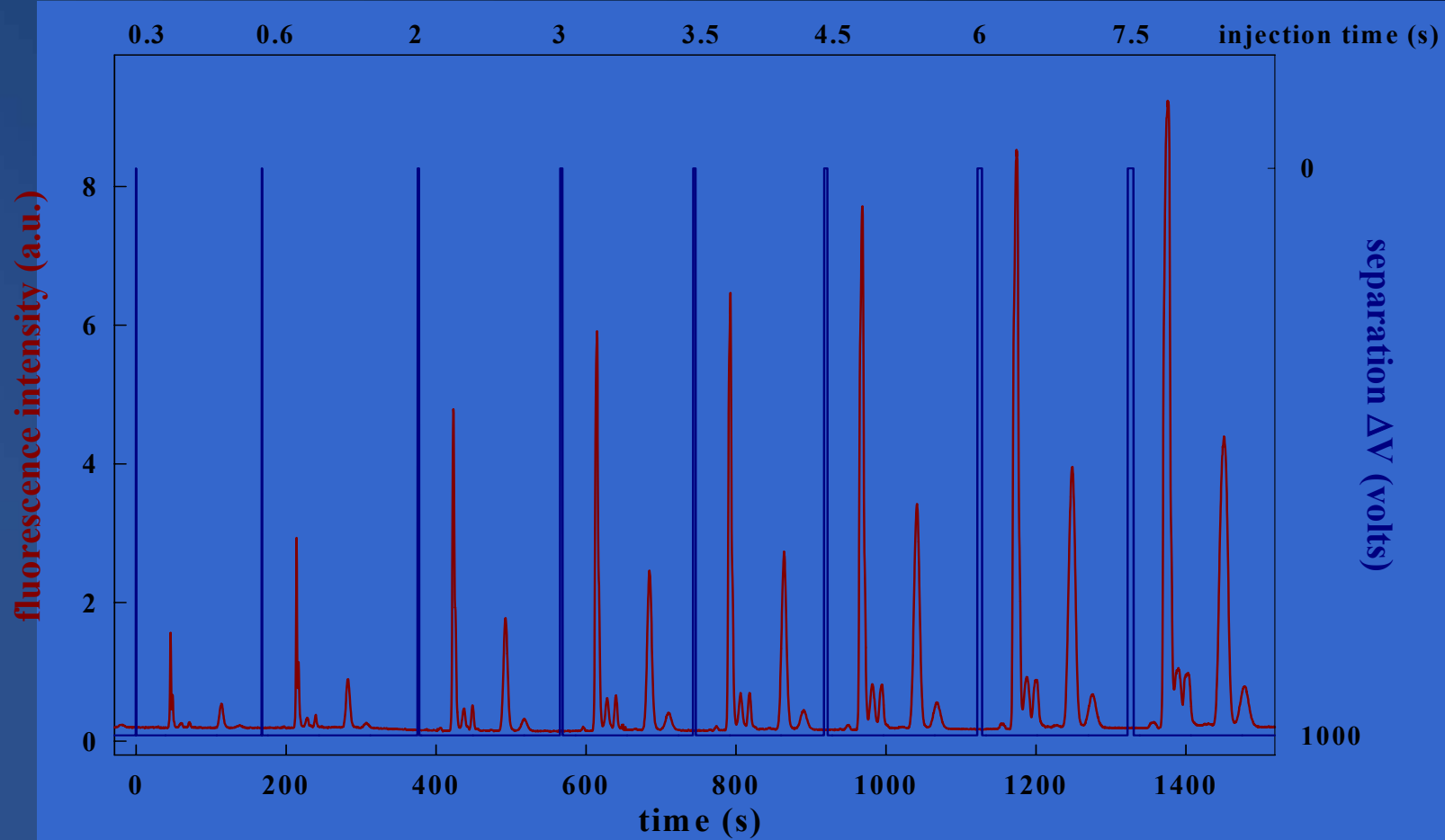
Challenges with Integrating Molecular Gates



Affinity to Specific Species: Integrating, controlling, and utilizing molecular recognition elements



Challenges with Integrating Molecular Gates



Transport & Separations: Strongly affected by different phenomena, e.g. chemical composition, molecular size, electrophoretic mobility.

Summary of Findings

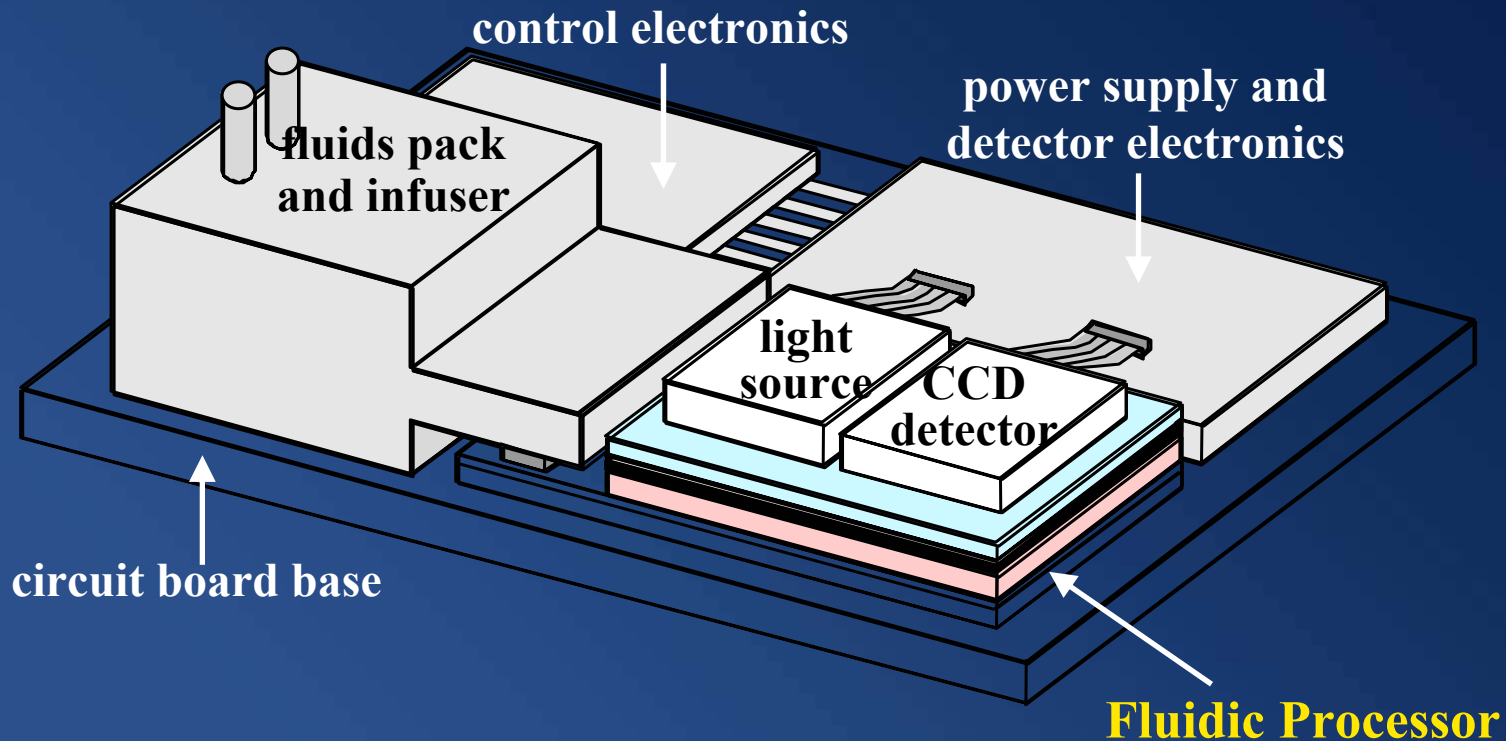
- 💧 ***Molecular Gates Create High-Electric Fields***
 - 💧 High fields (>10 KV/cm) for low voltages (>10 V)
- 💧 ***Collection mass efficiency near 100%***
 - 💧 Attomoles and smaller amounts can be collected
- 💧 ***Transport of Molecules***
 - 💧 Ion velocities high for mobility's 10^{-6} to $^{-4}$ cm^2/Vs
- 💧 ***Injection Velocities Lead to Rapid Mixing***
 - 💧 Fills injection volumes in milliseconds and within microns of the injection port.

Molecular gates allow rapid collecting, injecting, mixing, and reacting for μ TAS applications



Sensor work at UIUC

(Bohn, Lu, Shannon, Sweedler)



A fluidic processor, which exploits *both* **micro- and nanofluidics**, to manipulate **attomoles** of toxic species, such as *C. botulinum* neurotoxin A (BoNT/A), ppb of Pb, Hg, and ppt of polyaromatic hydrocarbons (NDMA).

What More is Needed With Water Issues Facing U.S.

- 💧 We need better information of aquifers (fresh *and* saline), quantities, flows, and constituents, and interconnection of watersheds
- 💧 Bold new research program on new methods to desalinate seawater *and* inland aquifers with waste residual management.
- 💧 New research in the science and technology of water purification for water reuse, contaminants removal, and disinfection.

BUT WE NEED THE PUBLIC, SCIENTISTS, AND POLICY MAKERS TO KNOW THE REAL VALUE OF WATER.



Future Directions

- Set a national Strategic Plan for water technology with *U.S. Strategic Water Initiative* (USSWI) for the next twenty years: Major USSWI Congress in New Orleans April 2008
- Need industrial input into strategic planning process
- Public/Private Partnership: billions to trillions at stake
- Build infrastructure to pilot plant ideas from research to create historical data needed to move bold new ideas into practice:

WE NEED A PIPELINE





How Can the U.S. Respond?

- A new, 10 year, multi-Agency program in the science and technology of water purification, including DOD, DOI, BOR, DHS, DOE, HHS, NSF, USDA, USEPA, USGS,...
- Development of public/private facilities for multiyear pilot and demonstration of treatment methodologies: Verification based on new accepted water source classes.
- Development of unified treatment modalities for categories of source waters and contaminants.



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?



Watershed Maps

- Aquifers, Rivers, Lakes & Usage for 2000
 - <http://nationalatlas.gov/atlasftp.html>
- State Boundaries, District Maps
 - ARC GIS Template Maps (USGS)
- Saline Aquifer Map
 - Desalination & Water Purification Technology Roadmap SNL& BoR (2003)



Water Withdrawal & Consumption Data

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

Water Use Projection Model Based on:

- ◆ Texas Water Development Board 2007 Plan and Projections

http://www.twdb.state.tx.us/publications/reports/State_Water_Plan/2007/2007StateWaterPlan/2007StateWaterPlan.htm

Energy Use & Water Nexus:

- ◆ Energy Demands On Water Resources: Report To Congress On The Interdependency Of Energy And Water, U.S. Department Of Energy, December 2006



Population Data

💧 Population Estimates

💧 U.S. Census Bureau County Population

<http://www.census.gov/popest/datasets.html>

💧 Population Projections

💧 U.S. Census Bureau Population Projections

<http://www.census.gov/population/www/projections/stproj.html>



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Some of the many people to thank who work so hard to accomplish the nearly impossible!



*water*CAMPUS