Wastewater as a Resource

Bioreactors & the Green Economy: Cycles, Networks, and Products

Bay Area Clean Water Agencies
Thursday, January 28, 2010

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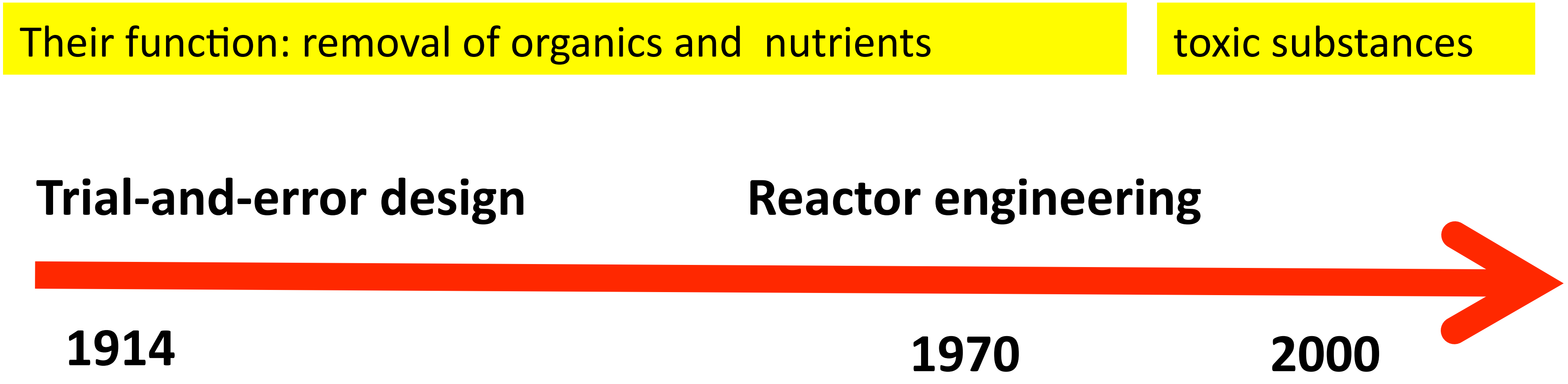
Stanford University

By the year 2000, there were more than 15,000 bioreactors treating wastewater in the US alone



Their function: removal of organics and nutrients

toxic substances

Trial-and-error design

Reactor engineering

1914

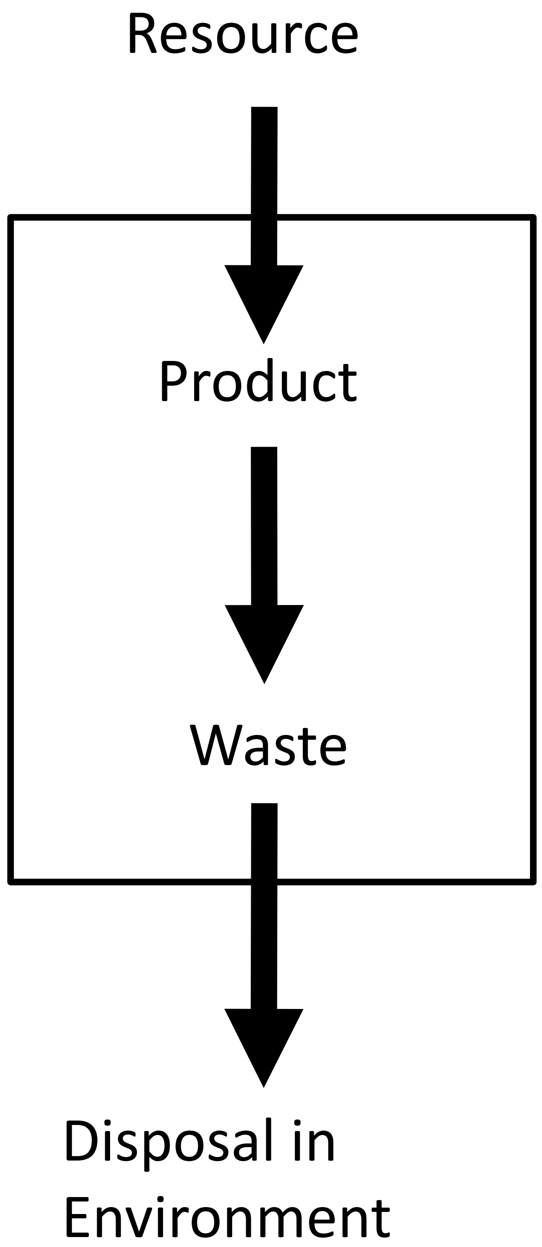
1970

2000

Life before 2000

- **Linear markets**
- **Cheap energy**
- **Climate change not on the radar**

Linear markets

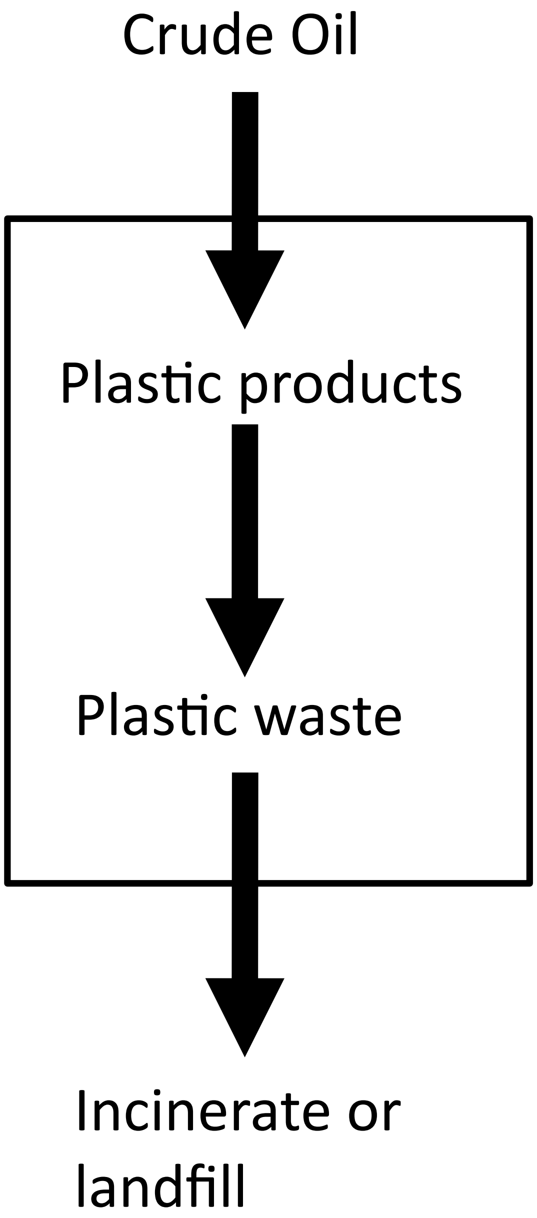


Resource

Product

Waste

Disposal in
Environment



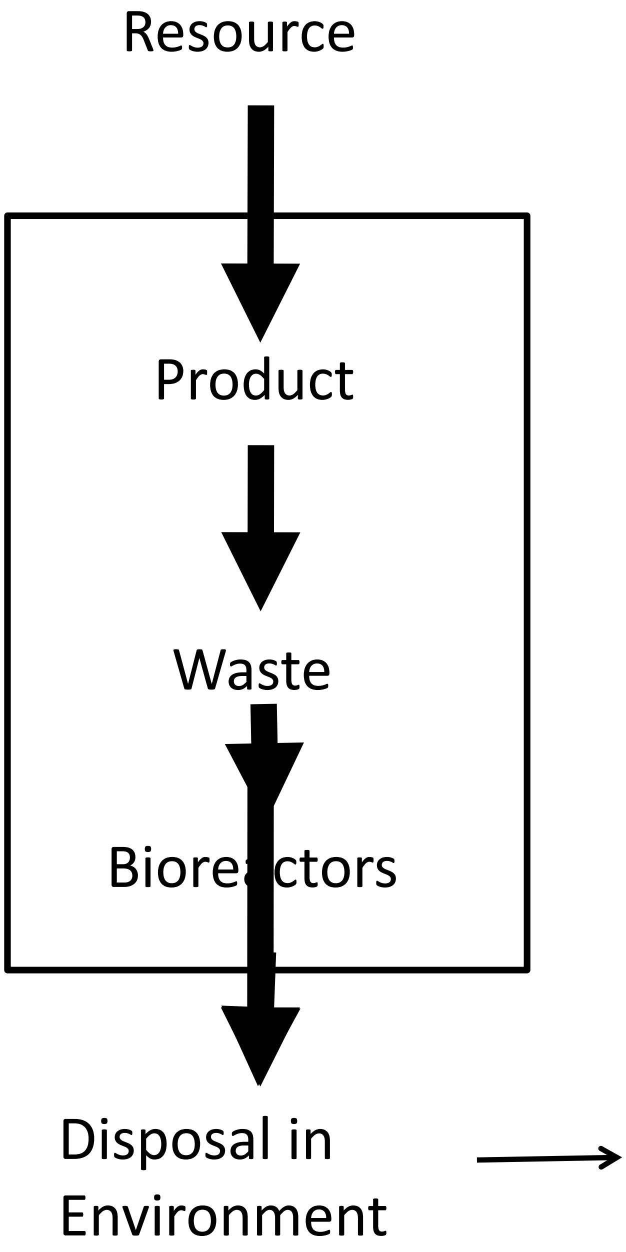
Crude Oil

Plastic products

Plastic waste

Incinerate or
landfill

Traditional function of bioreactors: protection of the environment & human health



Resource

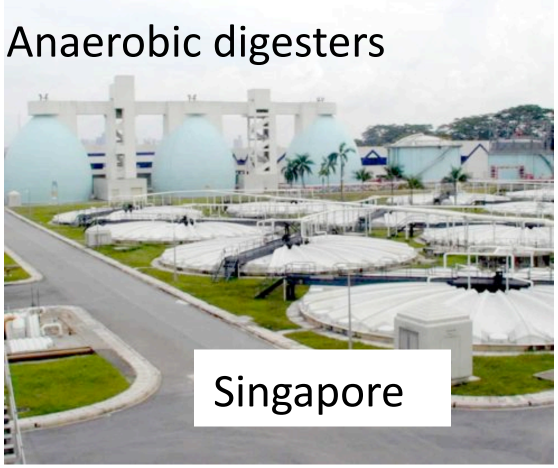
Product

Waste

Bioreactors

Disposal in Environment → Harm to environment and/or human health

Bioreactors provide a controlled environment for the growth and maintenance of complex, self-assembled microbial communities that perform ecologically critical functions.

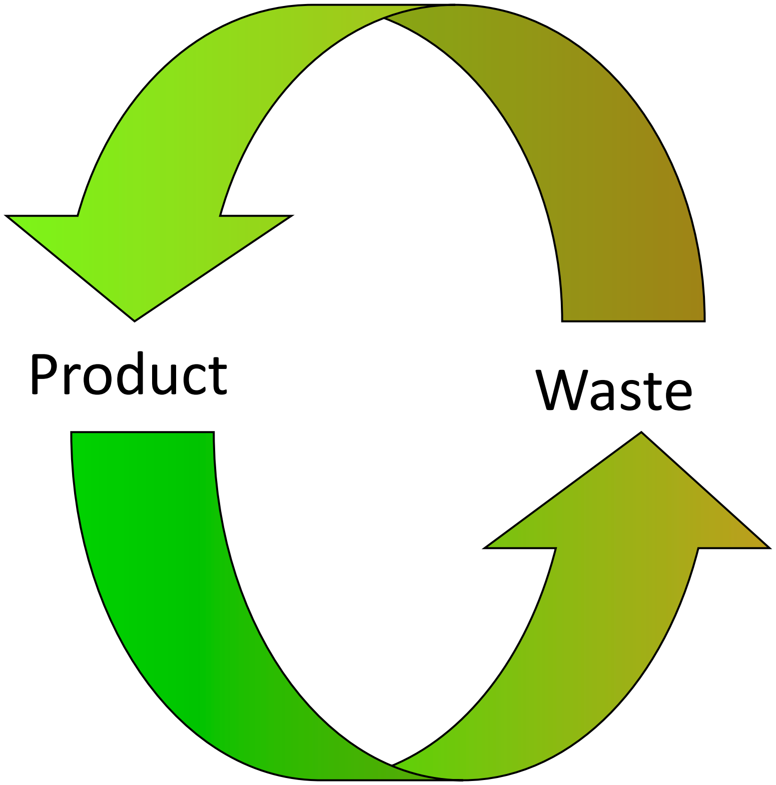


Landfills can be operated as anaerobic bioreactors for production of methane

Courtesy of Waste Management

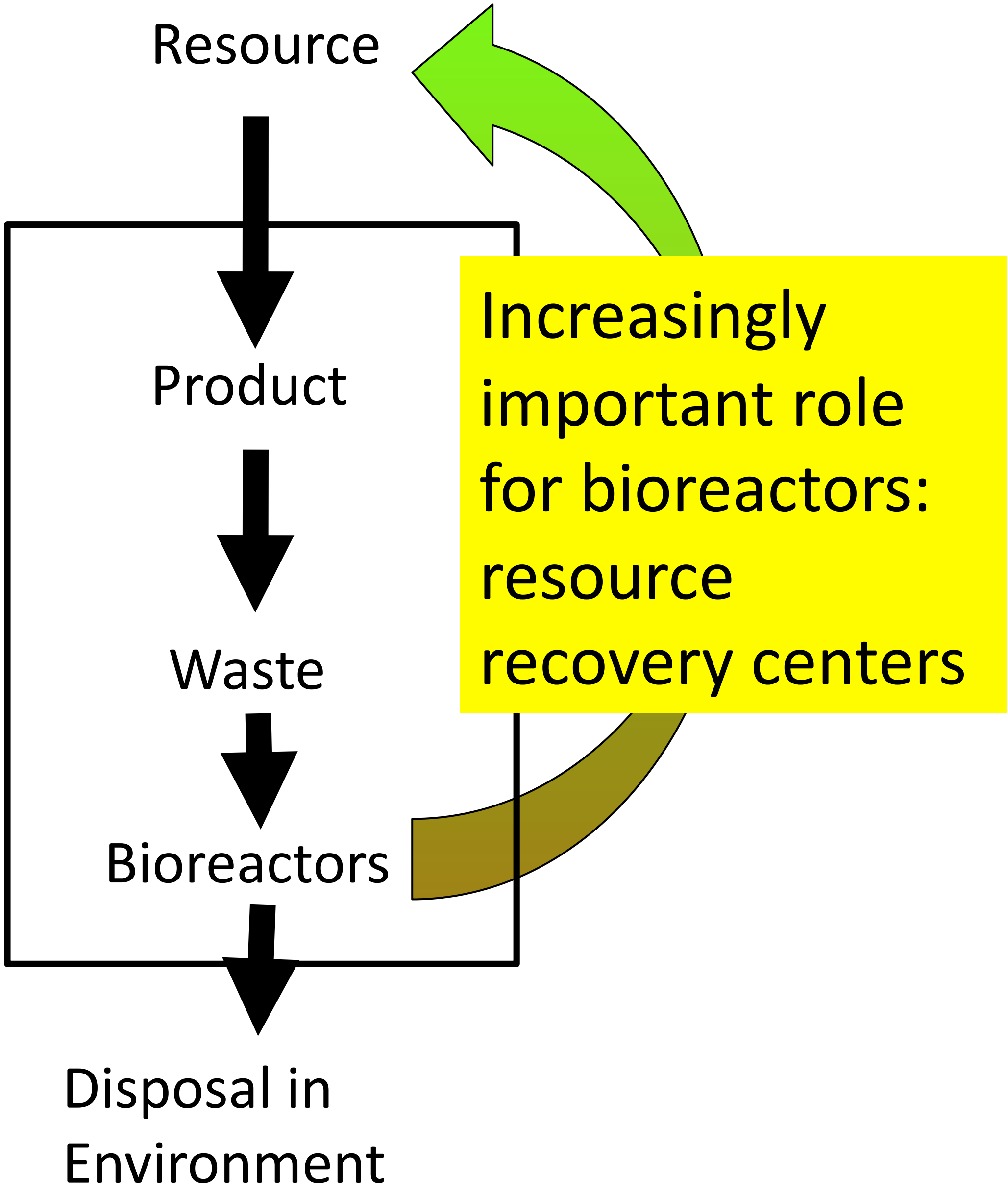
Alternative to linear markets

Ecology-based Markets



Product

Waste



Resource

Product

Waste

Bioreactors

Disposal in Environment

Increasingly important role for bioreactors: resource recovery centers

Wastewater as a resource

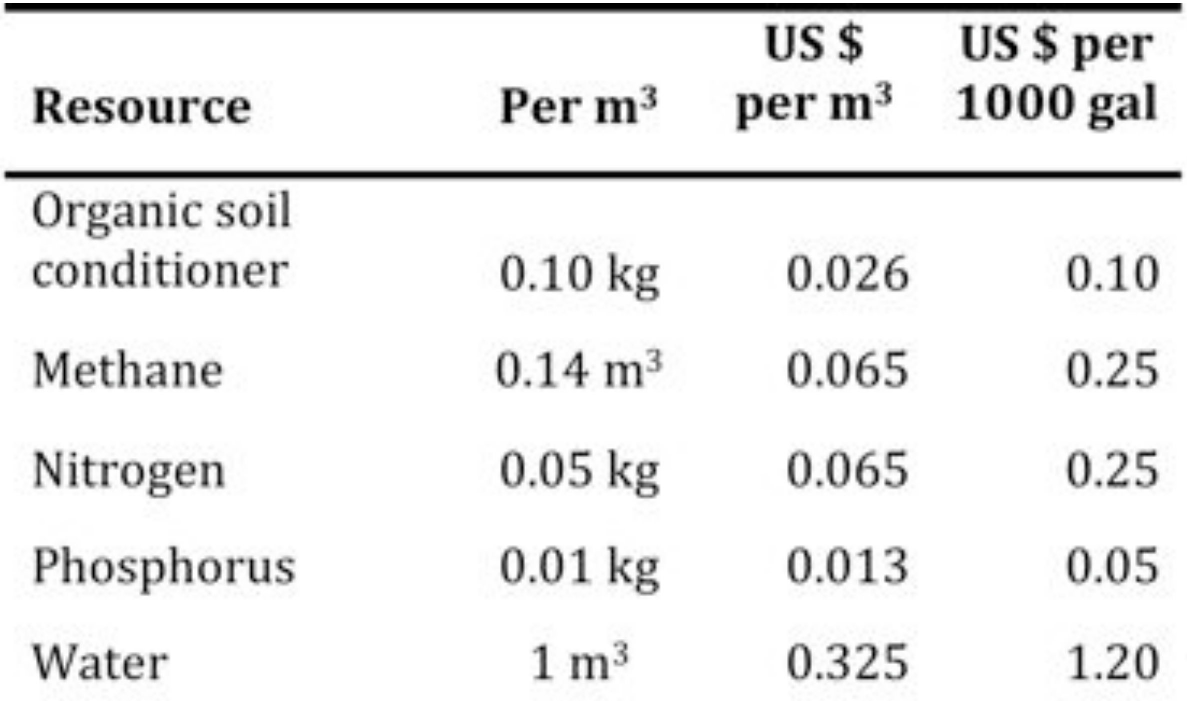
Useful products!

Components of wastewater:

- Water (99.9%)
- Biodegradable organics
- Nutrients (N and P)

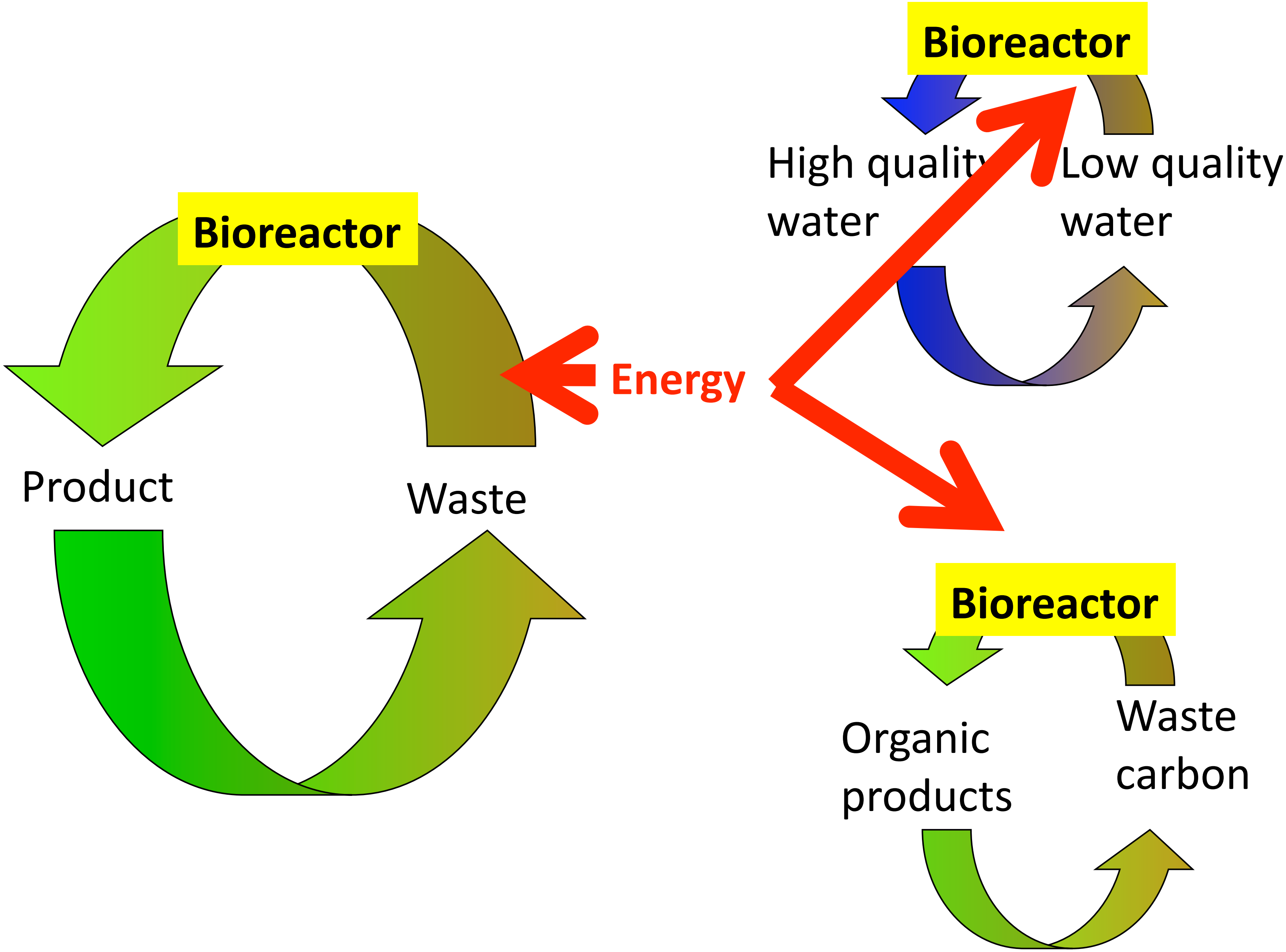
- Pathogens
- Salt
- Refractory organics

The economic value of the resource



Resource	Per m^3	US \$ per m^3	US \$ per 1000 gal
Organic soil conditioner	0.10 kg	0.026	0.10
Methane	0.14 m^3	0.065	0.25
Nitrogen	0.05 kg	0.065	0.25
Phosphorus	0.01 kg	0.013	0.05
Water	1 m^3	0.325	1.20

From Willy Verstraete (2008)



Bioreactor

Product

Waste

Energy

Bioreactor

High quality water

Low quality water

Bioreactor

Organic products

Waste carbon

Requirements

- Products from waste
  (a closed loop)
- Low net energy demand (input-output)
- Match between supply and demand for product

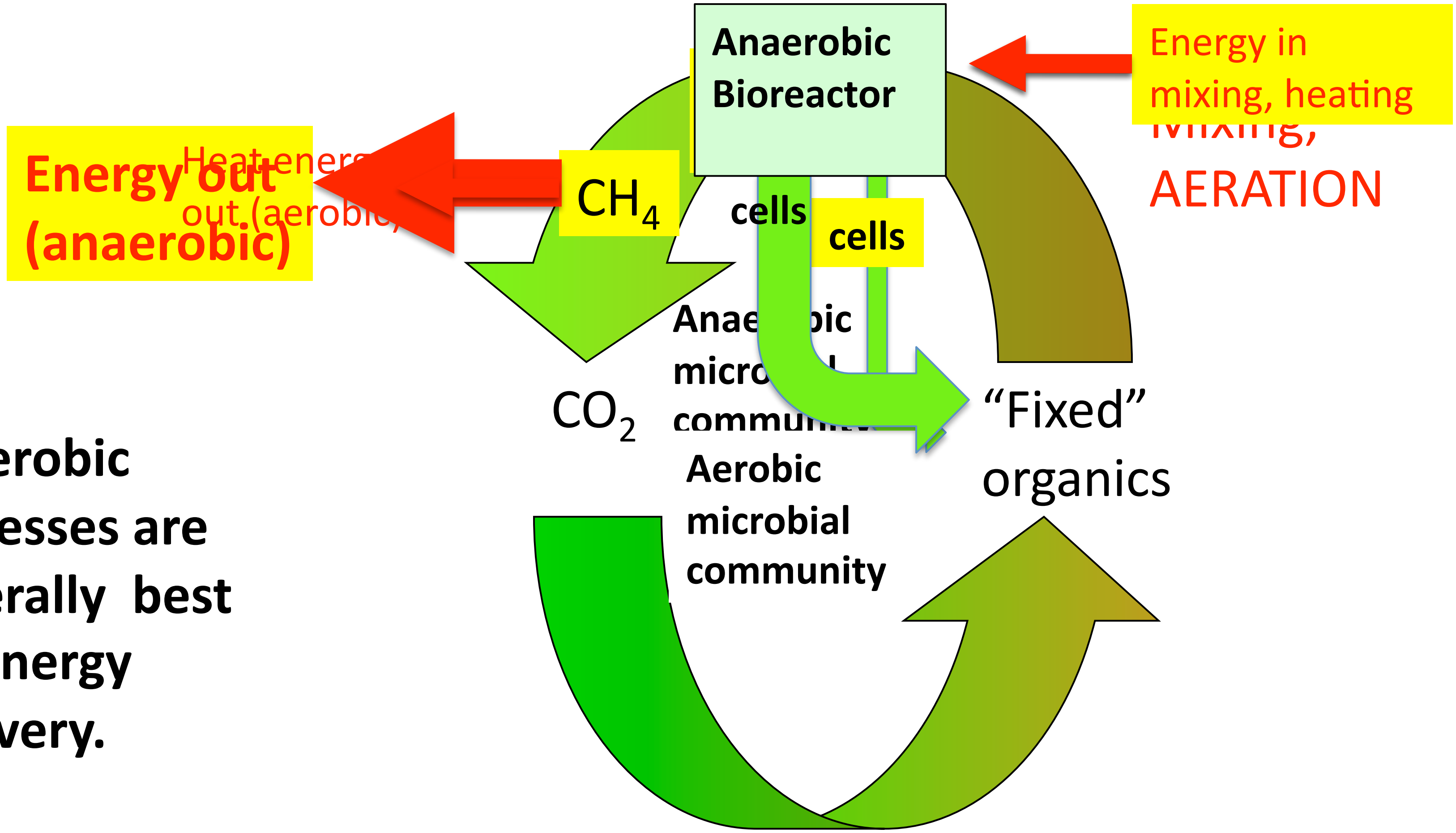
How can we achieve low net energy input?

Recover energy from waste

Minimize energy for materials transport

Use “short-circuit” cycles to our advantage

How can we best recover energy?



Energy out (anaerobic)

Heat energ out (aerobic

CH$_4$

Anaerobic Bioreactor

Energy in mixing, heating

Mixing,

AERATION

cells

cells

Anae bic micro l communit

CO$_2$

“Fixed” organics

Aerobic microbial community

Anaerobic processes are generally best for energy recovery.

How can we best minimize energy for transport?

Locate reactors close to markets for products.

Move materials that require the least energy to move

electrons<gases

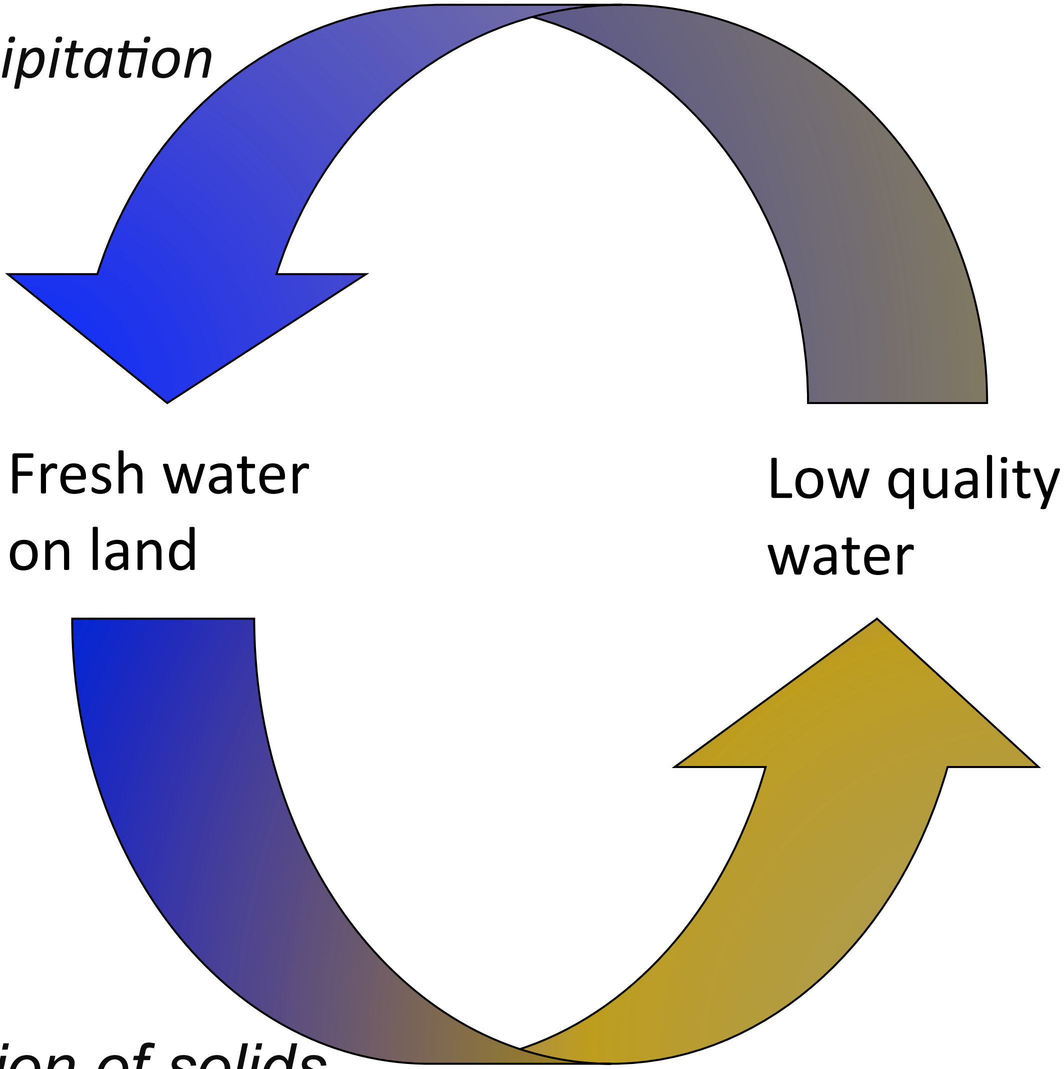
<liquids<solids

Take advantage of existing conveyance systems (Internet, gas pipelines, sewers, etc.)

- **The Water Cycle**

Natural cycle “turns” at 107,000 km^3/yr.

We use only 1,600 km^3/yr.



Evapotransporation

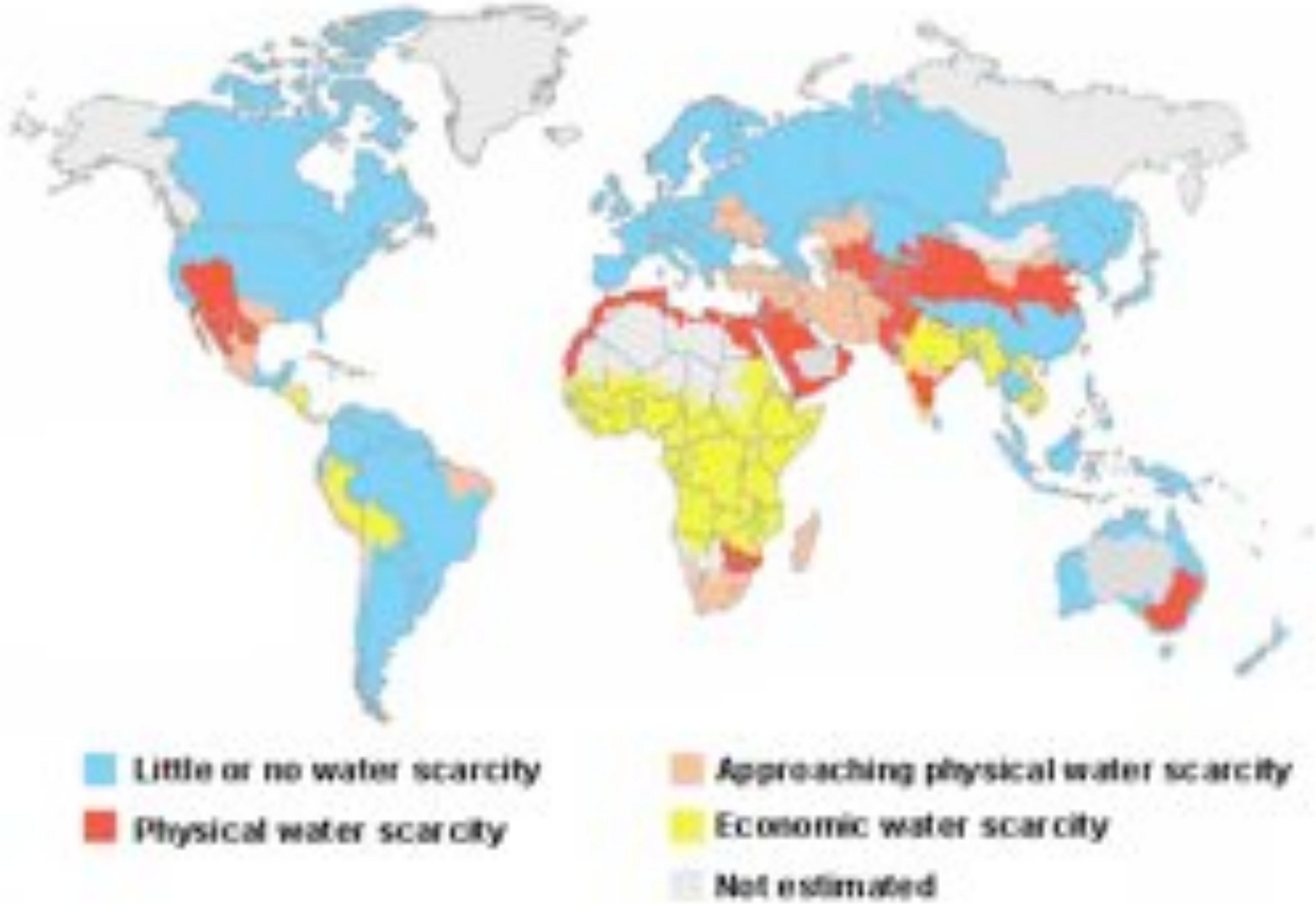
Precipitation

Fresh water on land

Low quality water

Dissolution of solids
Salination

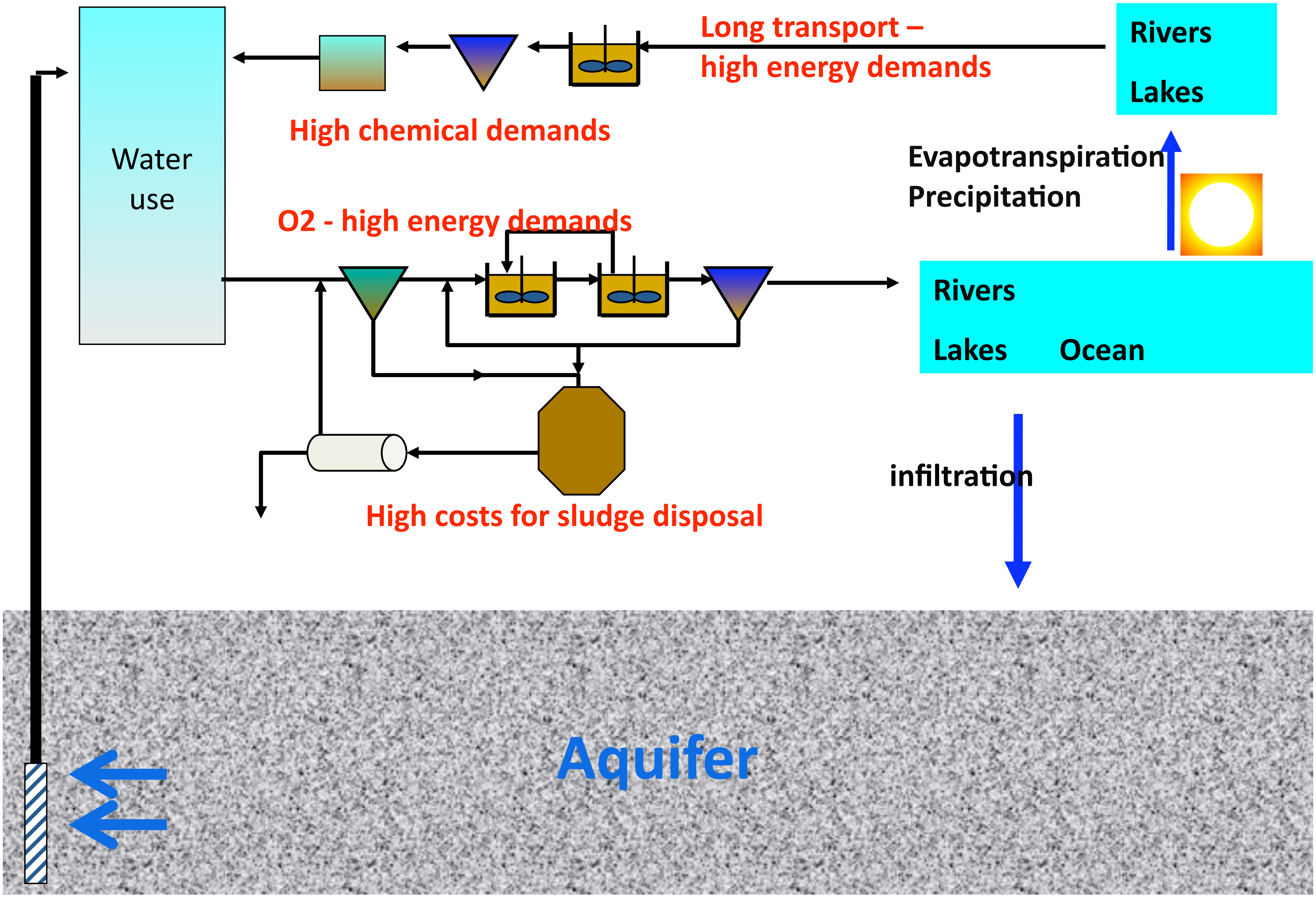
The problem is distribution



Source: Rogers, P. 2008. Facing the Freshwater Crisis. *Scientific American. August 2008 On-line supplement.* http://www.sciam.com/article.cfm?id=freshwater-crisis-current-situation.

Conventional water cycle

Can we improve it?



Water use

Long transport –
high energy demands

Rivers

Lakes

High chemical demands

Evapotranspiration
Precipitation

O2 - high energy demands

Rivers

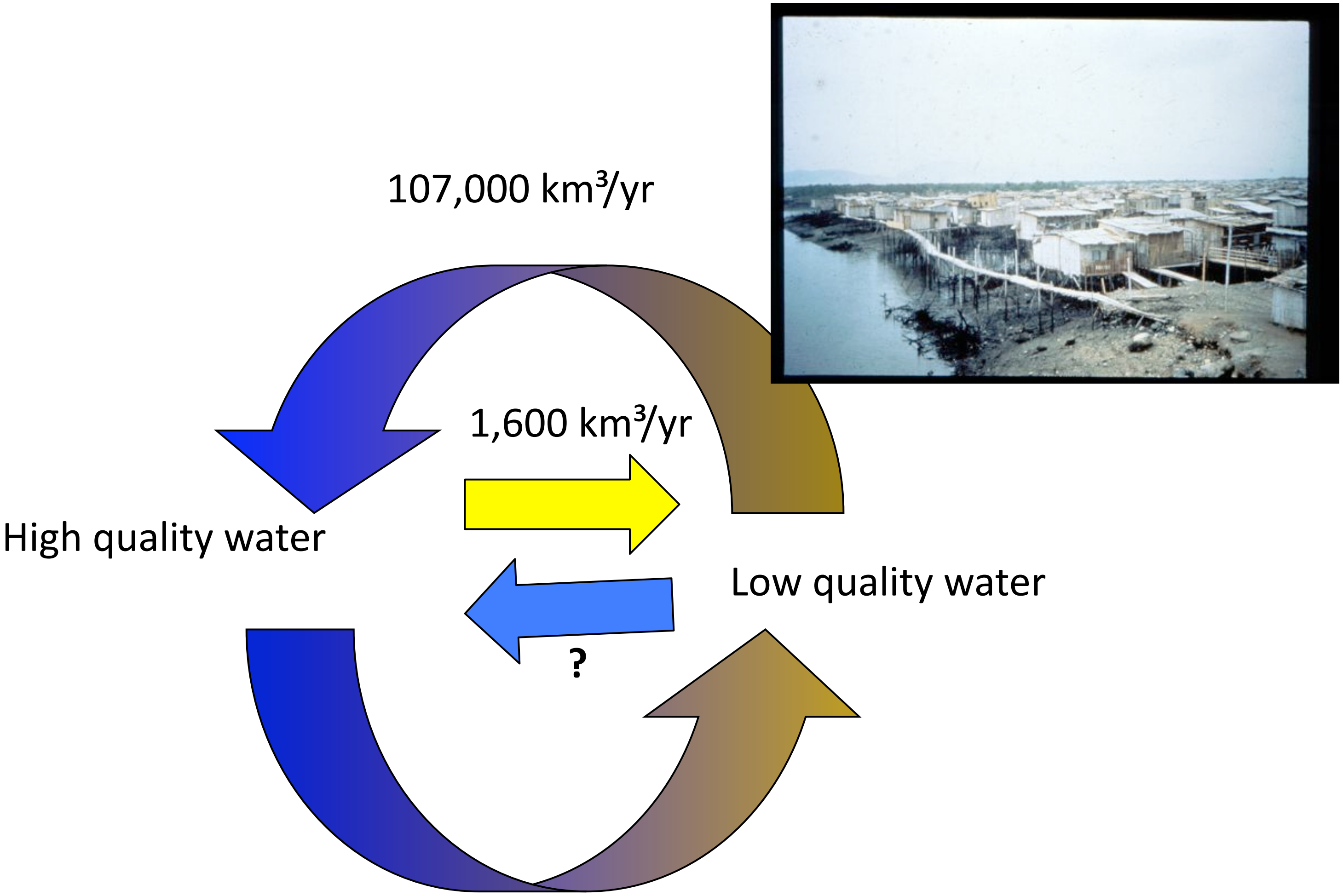
Lakes Ocean

infiltration

High costs for sludge disposal

Aquifer

How can we short-circuit the water cycle?



107,000 km³/yr

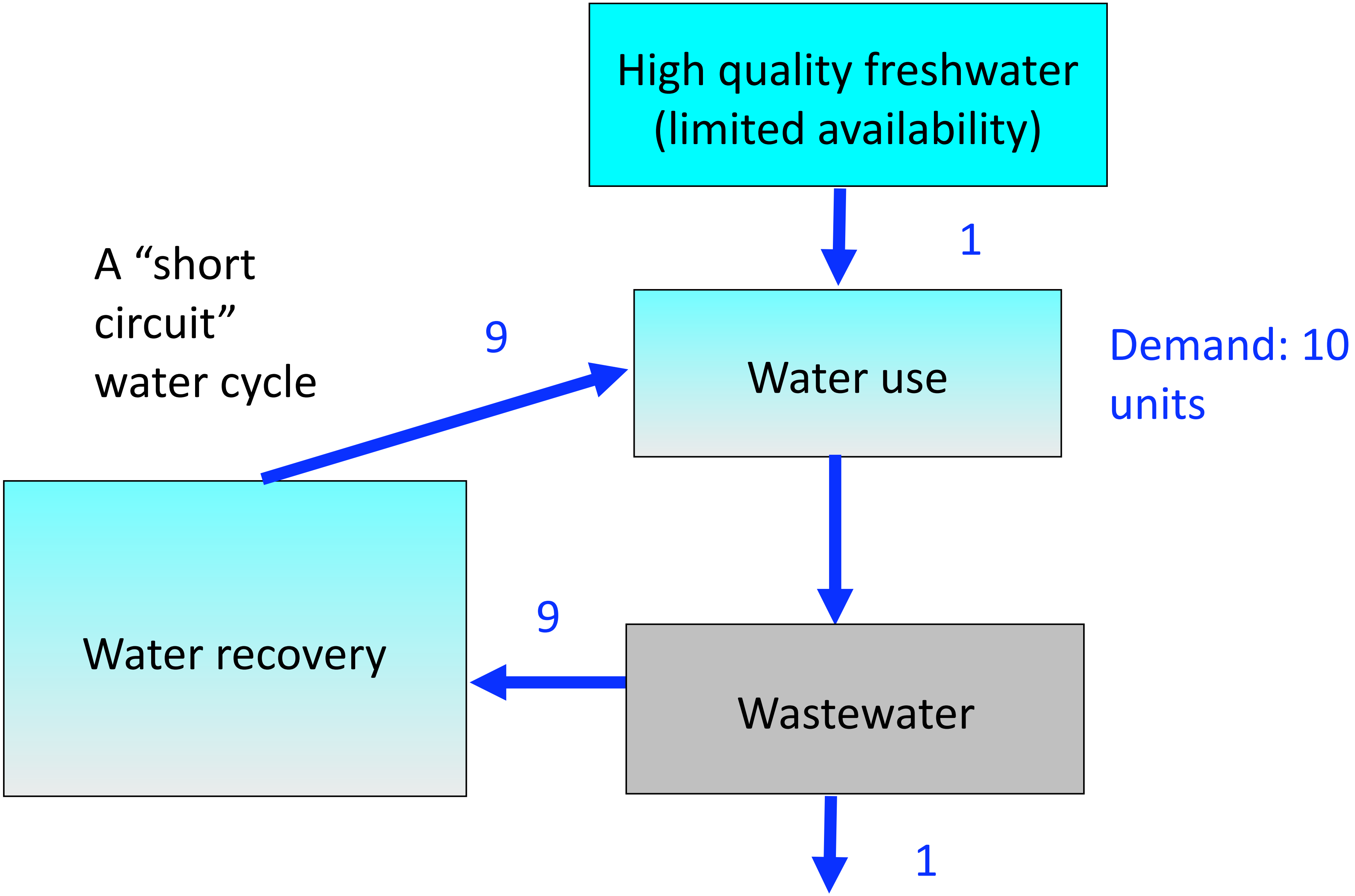
1,600 km³/yr

High quality water

Low quality water

?

Traditional linear water market



High quality freshwater
(limited availability)

1

A “short
circuit”
water cycle

9

Water use

Demand: 10
units

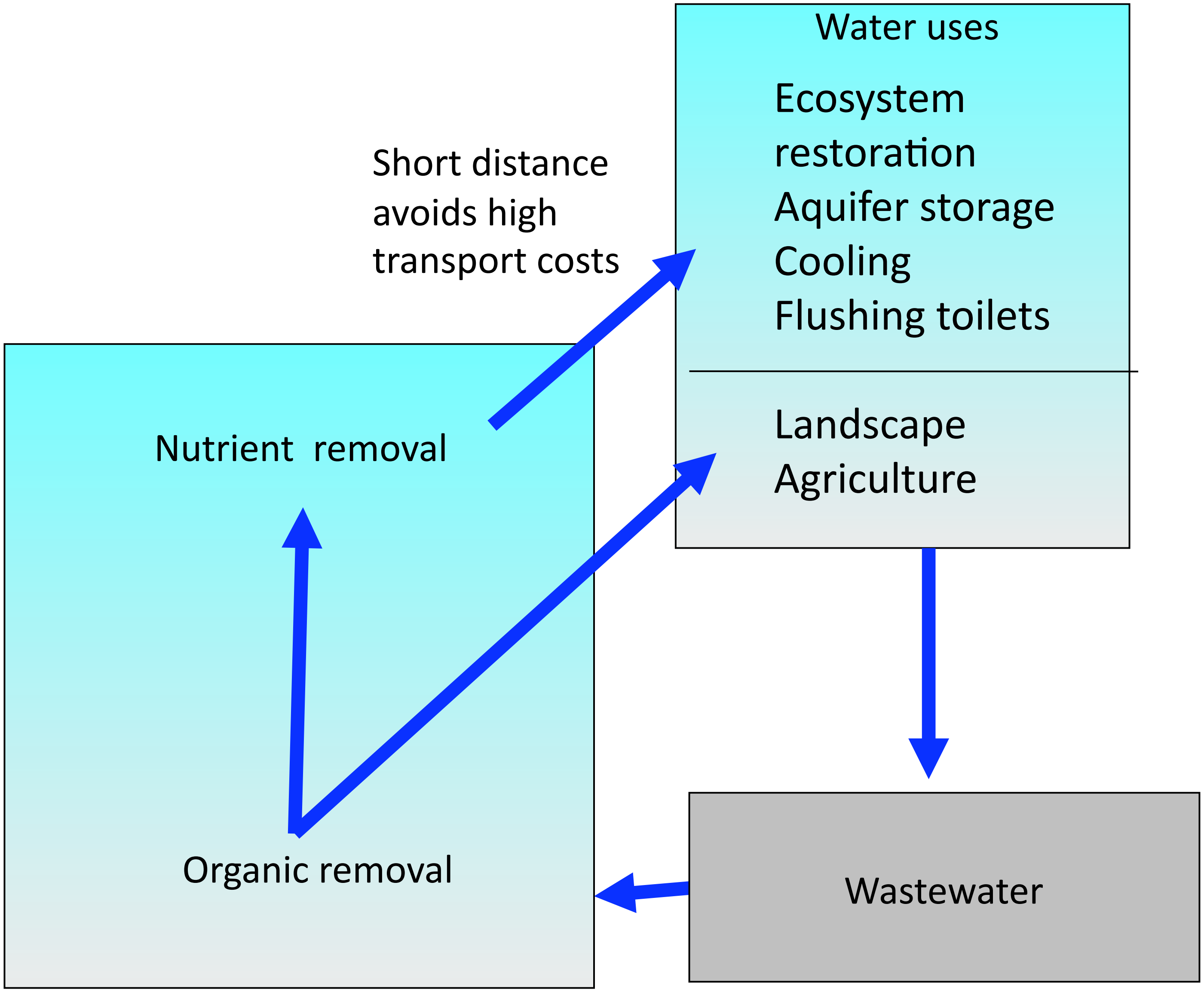
9

Water recovery

Wastewater

1

A short-circuit water cycle



Short distance
avoids high
transport costs

Water uses

Ecosystem
restoration
Aquifer storage
Cooling
Flushing toilets

Landscape
Agriculture

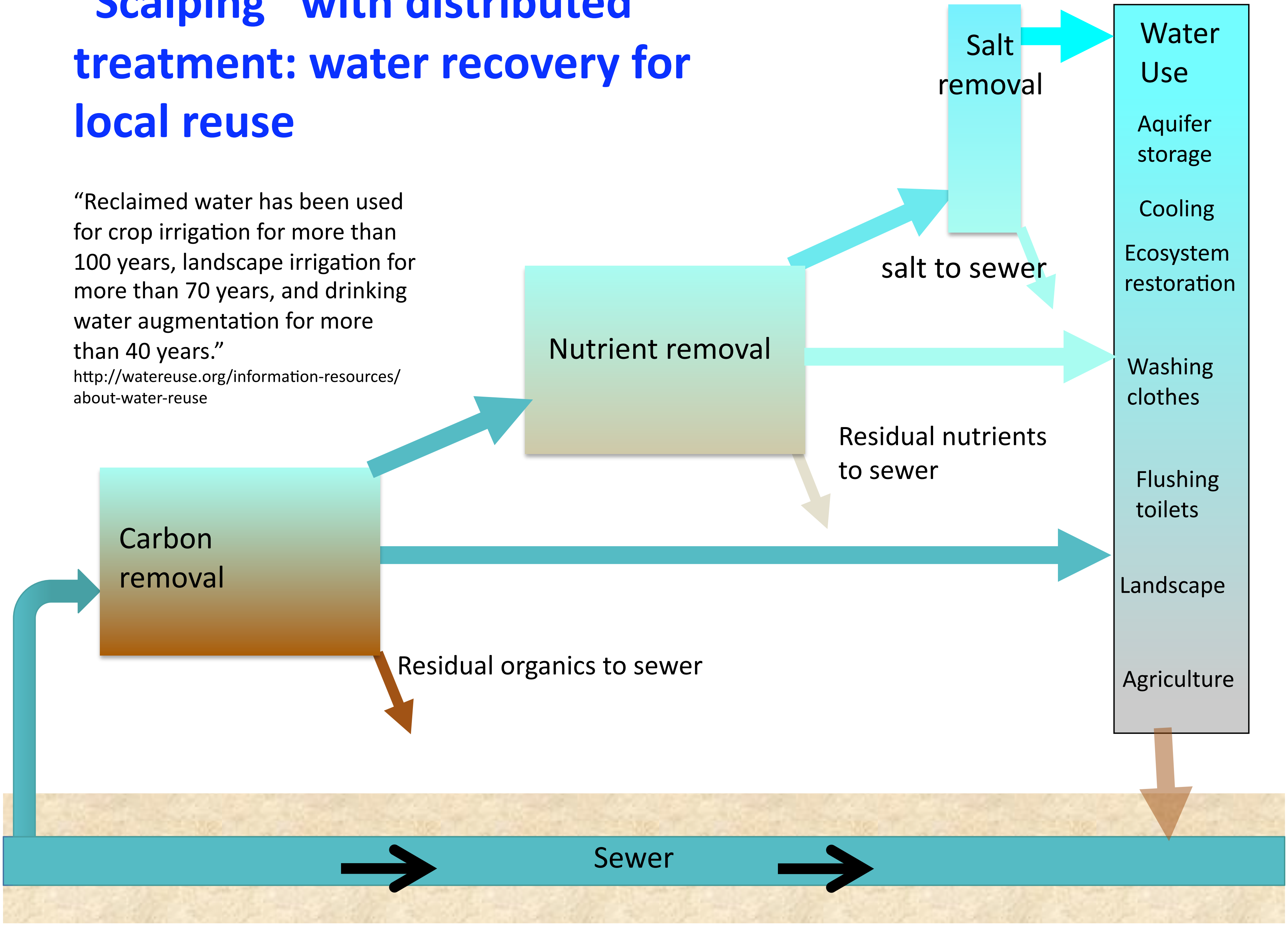
Nutrient removal

Organic removal

Wastewater

“Scalping” with distributed treatment: water recovery for local reuse

“Reclaimed water has been used for crop irrigation for more than 100 years, landscape irrigation for more than 70 years, and drinking water augmentation for more than 40 years.”
http://watereuse.org/information-resources/about-water-reuse



Salt removal

Water Use

Aquifer storage

Cooling

Ecosystem restoration

salt to sewer

Nutrient removal

Washing clothes

Residual nutrients to sewer

Flushing toilets

Carbon removal

Landscape

Residual organics to sewer

Agriculture

Sewer

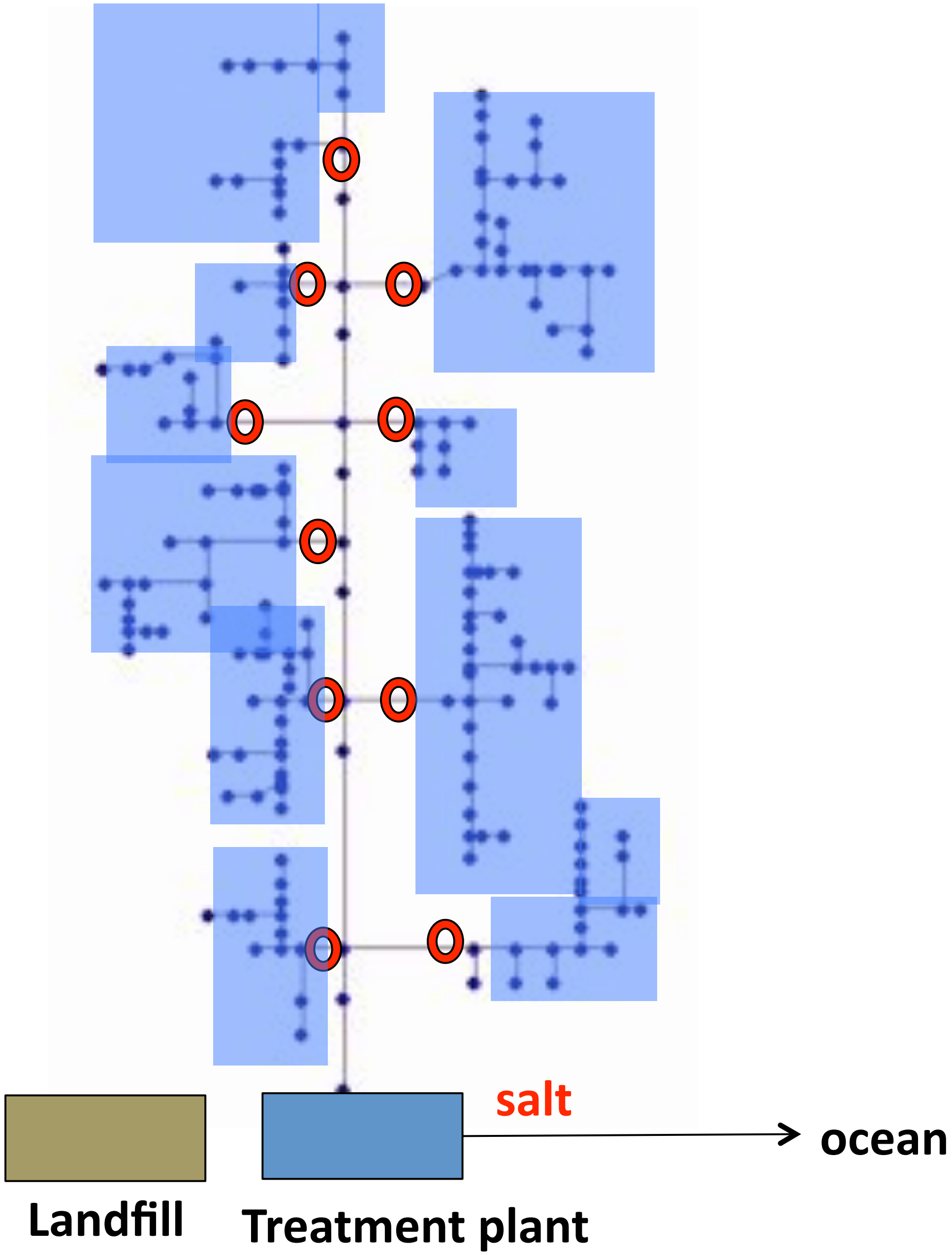
For the Stanford campus, “scalping” is a potential supply of non-potable water. Recovery of water at $1/1000 gallons would be a good goal.

Widespread “scalping” would change the composition of the water to be treated at the centralized facility.

Distributed scalping facilities for local water reuse

○ Scalping facilities

🟦 Harvest water


salt

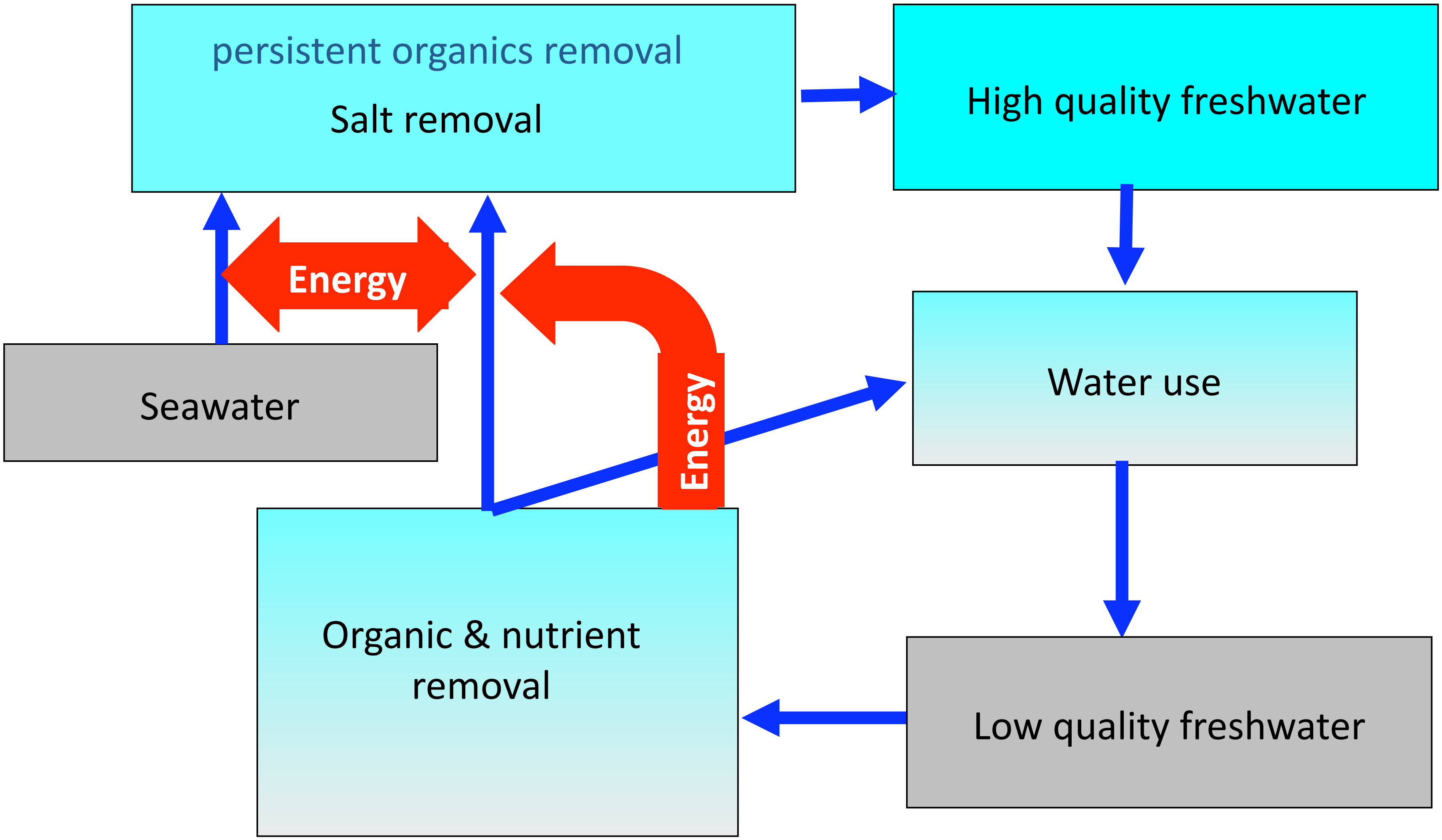
ocean

Landfill

Treatment plant

Poul Harremoes

“Water can be treated to any degree of purity at ever increasing cost”



persistent organics removal

Salt removal

High quality freshwater

Energy

Seawater

Energy

Water use

Organic & nutrient removal

Low quality freshwater

Energy for salt removal

Biologically-treated wastewater effluent vs. seawater

Thermodynamic limit = RTC
Seawater - (0.0821 atm/M-K)(298K)(1 M) = 24 atm
Wastewater effluent = (0.0821 atm/M-K)(298K)(0.05 M) = 1.2 atm

Current reverse osmosis technology
Seawater = 55 atm
Wastewater effluent <10.5 atm

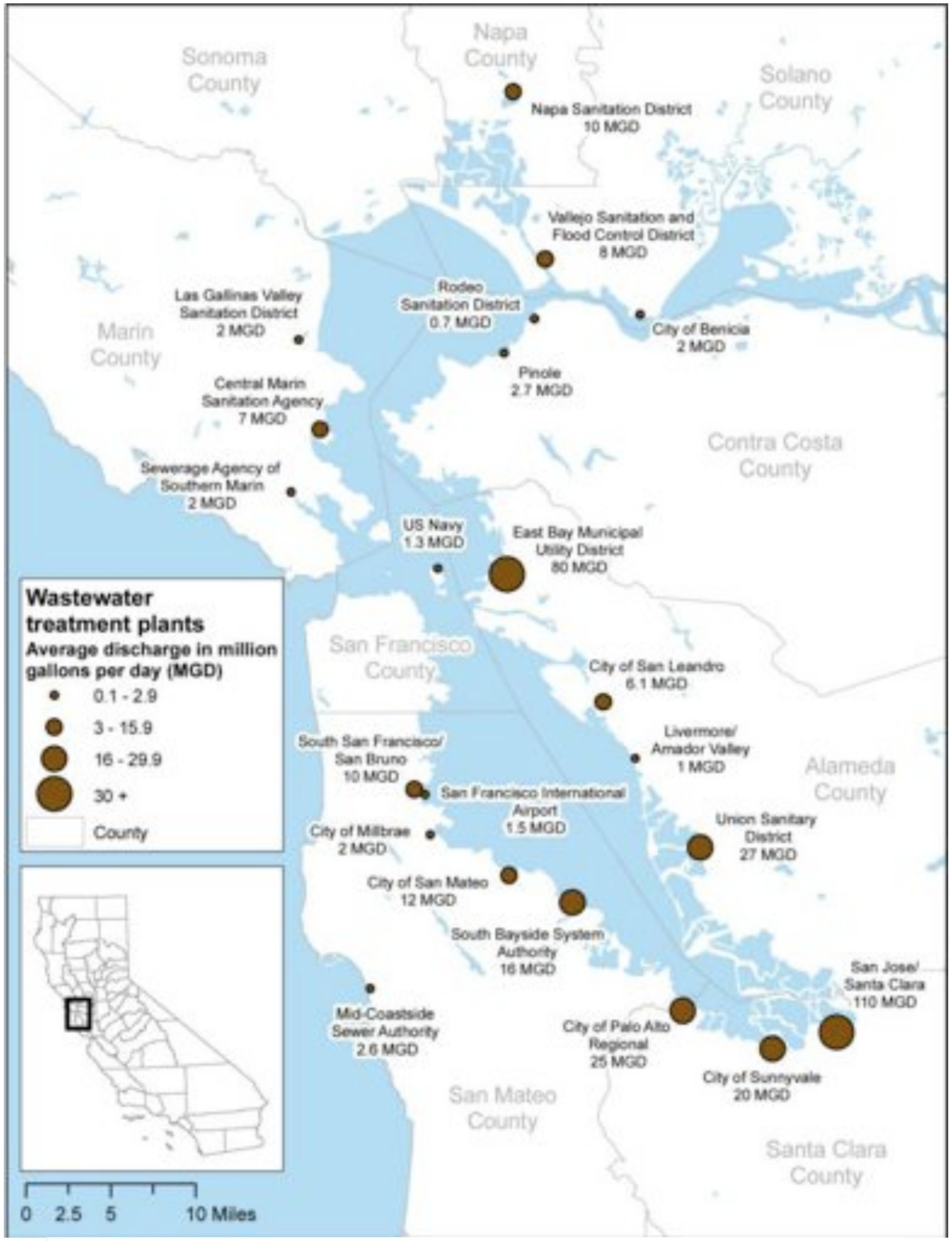
Biologically-treated wastewater has a huge advantage.

The key: bioreactors that enable low-cost, low-energy C and N removal.

Another reason to consider distributed treatment and reuse: sea level rise & flooding

21 wastewater treatment plants in the SF Bay are susceptible to a 100-year 1.4-m coastal flood on the San Francisco Bay

Heberger, M., H. Cooley, P. Herrera, P. H. Gleick, and E. Moore. 2009. The Impacts of Sea-level Rise on the California Coast. California Climate Change Center. P. 62.

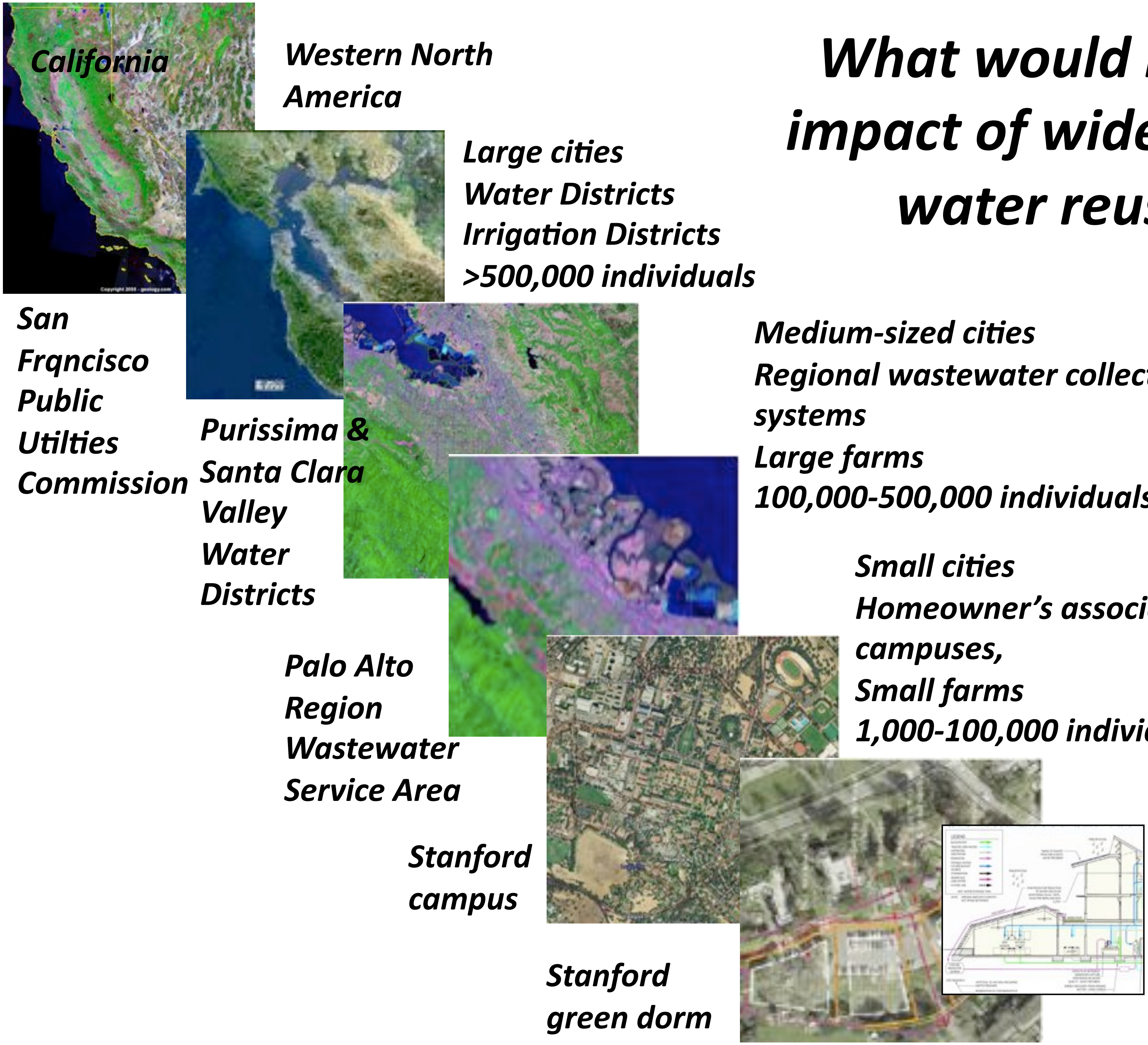


San Francisco Bay wastewater treatment plants vulnerable to a 100-year coastal flood with a 1.4-meter sea-level rise

Data sources: USGS/Scripps Institution of Oceanography, EPA PCS Database, CaSIL, ESRI.
http://www.pacinst.org/reports/sea_level_rise

PACIFIC INSTITUTE

What would be the impact of widespread water reuse?



Western North America

Large cities
Water Districts
Irrigation Districts
>500,000 individuals

San Frqncisco Public Utilties Commission

Medium-sized cities
Regional wastewater collection systems
Large farms
100,000-500,000 individuals

Purissima & Santa Clara Valley Water Districts

Small cities
Homeowner's associations, campuses,
Small farms
1,000-100,000 individuals

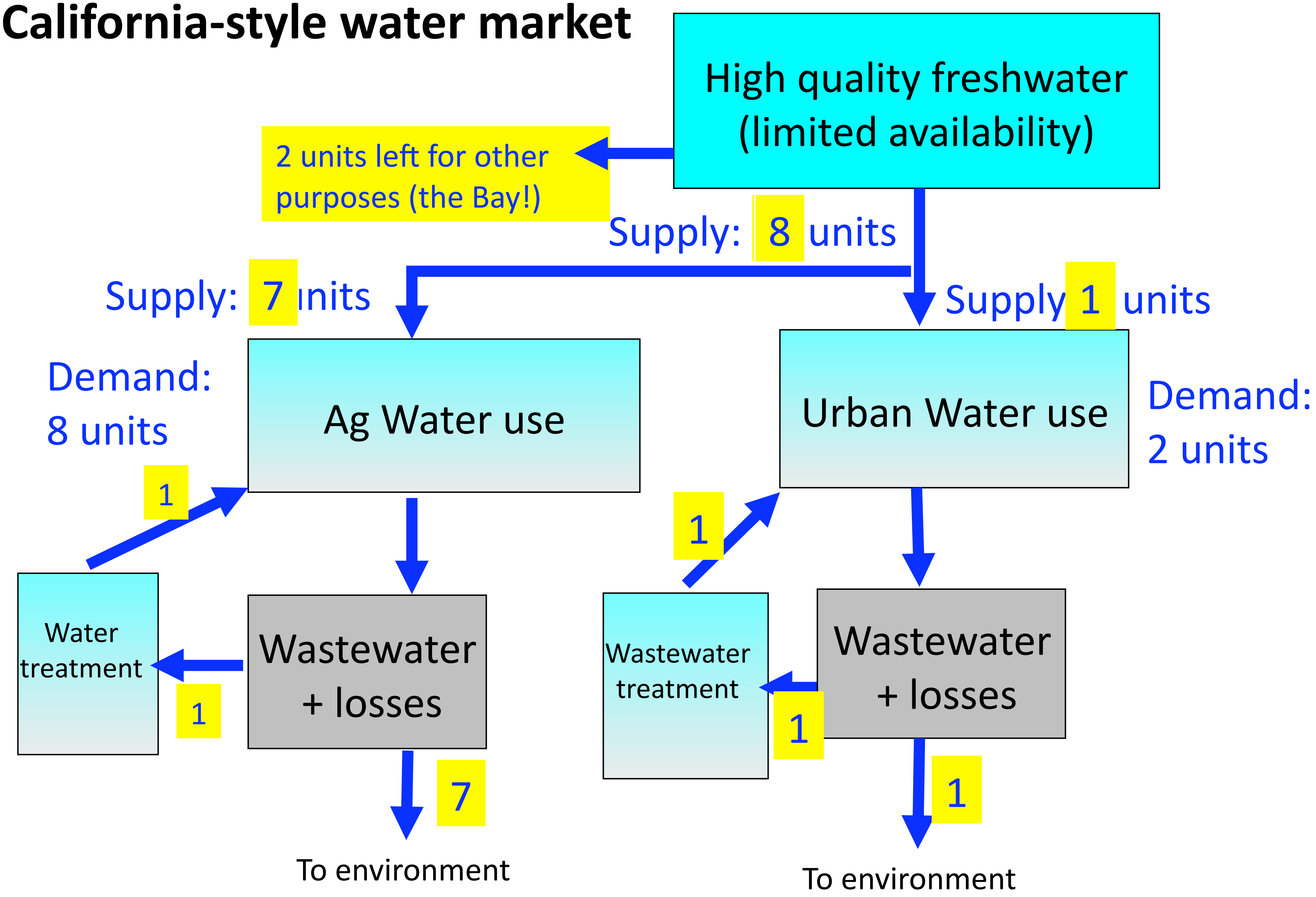
Palo Alto Region Wastewater Service Area

Stanford campus

Buildings (Hotels, Dorms, etc.)
10-1,000 individuals

Stanford green dorm

California-style water market



High quality freshwater (limited availability)

2 units left for other purposes (the Bay!)

Supply: 8 units

Supply: 7 units

Supply 1 units

Demand: 8 units

Ag Water use

Urban Water use

Demand: 2 units

1

1

Water treatment

1

Wastewater + losses

Wastewater treatment

1

Wastewater + losses

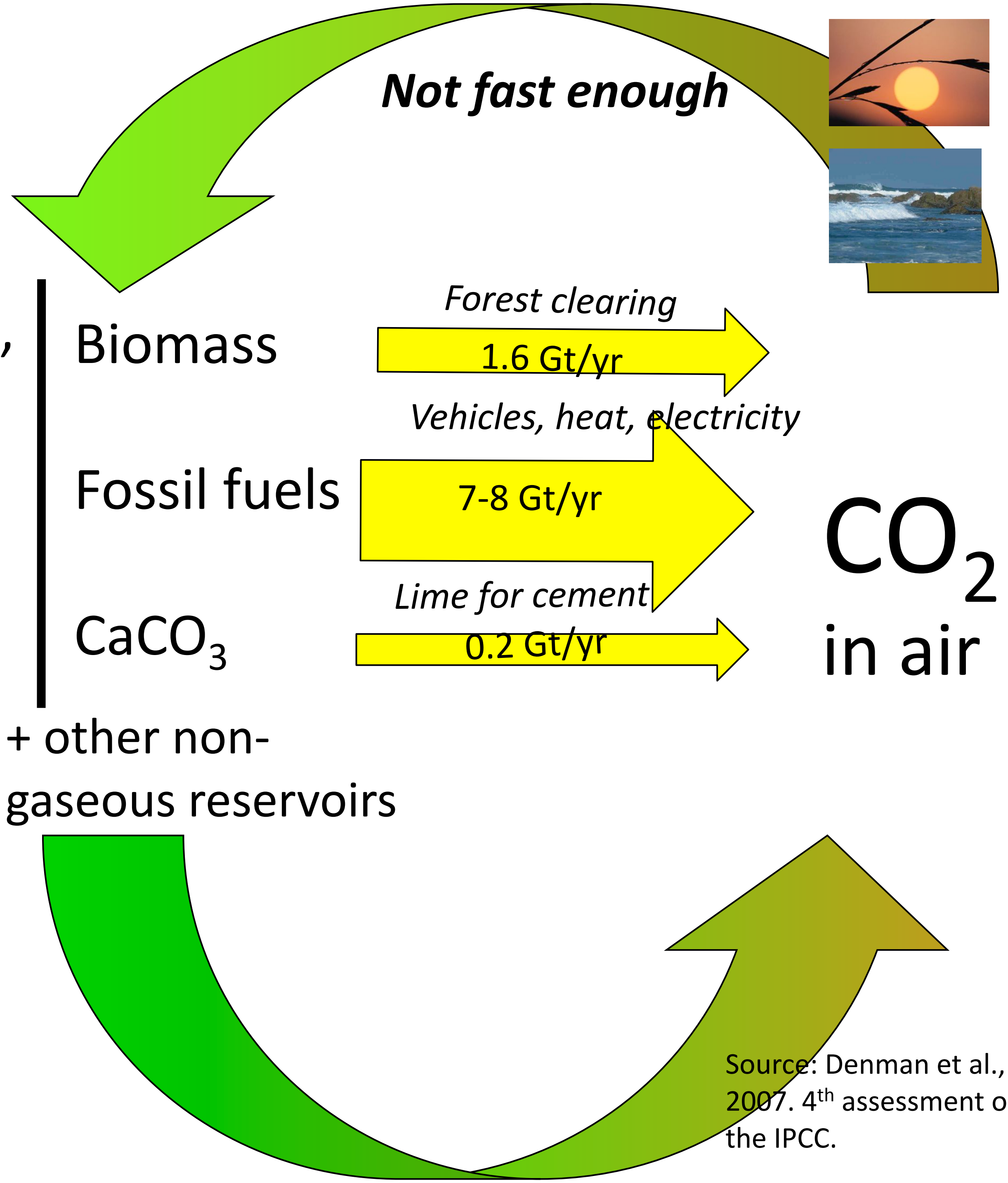
7

1

To environment

To environment

The Carbon Cycle



Not fast enough

“Fixed Carbon”

Biomass

Fossil fuels

$CaCO_3$

+ other non-gaseous reservoirs

Forest clearing

1.6 Gt/yr

Vehicles, heat, electricity

7-8 Gt/yr

Lime for cement

0.2 Gt/yr

CO_2 in air

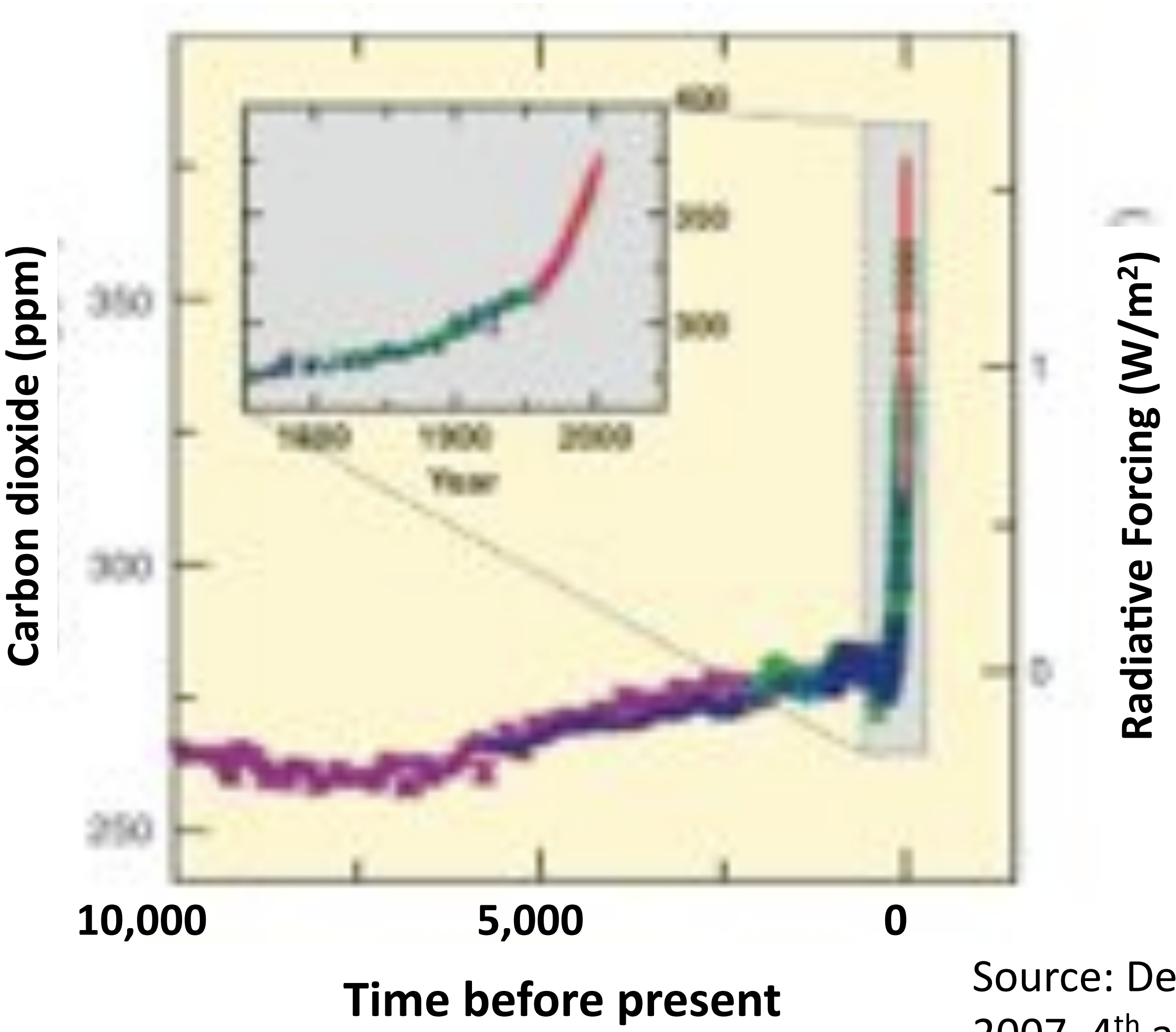
Pre-industrial cycle was spinning at 190 Gt C/yr

Human emissions have short-circuited the cycle, adding about 10 Gt C/yr.

1 Gt = 10^9 metric tons
= 1 Petagram

Source: Denman et al., 2007. 4th assessment of the IPCC.

Change in CO_2 levels in the atmosphere over the past 10,000 years



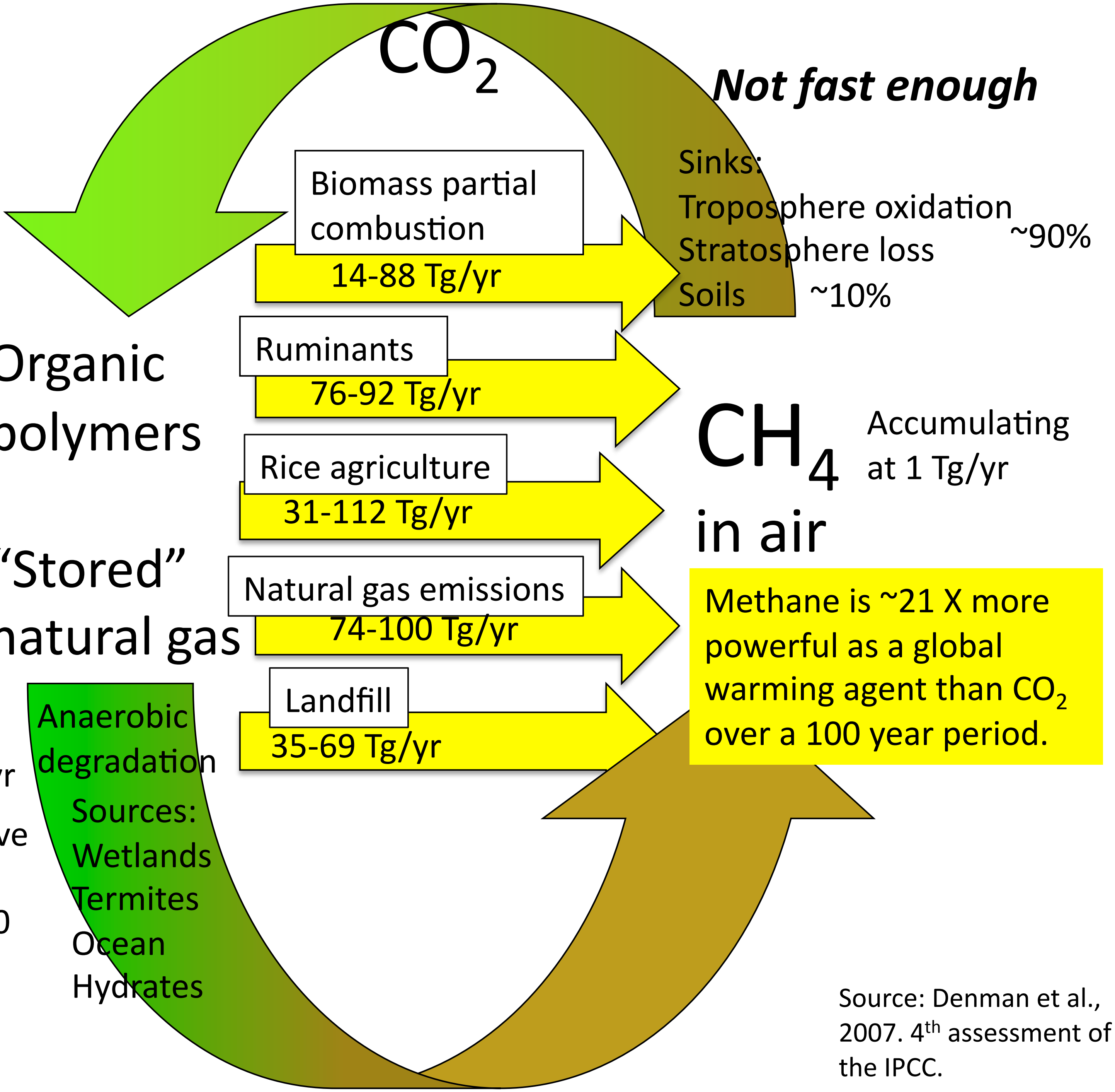
Source: Denman et al., 2007. 4th assessment of the IPCC.

At 450 ppm CO_2 "we will trigger potentially irreversible glacial melt & sea level rise out of humanity's control"

Source: UN Intergovernmental Panel on Climate Change (IPCC)

At the current CO_2 accumulation rates, we will reach 450 ppm by 2035-2040.

The methane ”cycle”



CO_2

Not fast enough

Sinks:
Troposphere oxidation
Stratosphere loss ~90%
Soils ~10%

Biomass partial combustion
14-88 Tg/yr

Ruminants
76-92 Tg/yr

Rice agriculture
31-112 Tg/yr

Natural gas emissions
74-100 Tg/yr

Landfill
35-69 Tg/yr

CH_4 in air

Accumulating at 1 Tg/yr

Methane is ~21 X more powerful as a global warming agent than CO_2 over a 100 year period.

“Fixed Methane”

Organic polymers

“Stored” natural gas

Anaerobic degradation

Sources:
Wetlands
Termites
Ocean
Hydrates

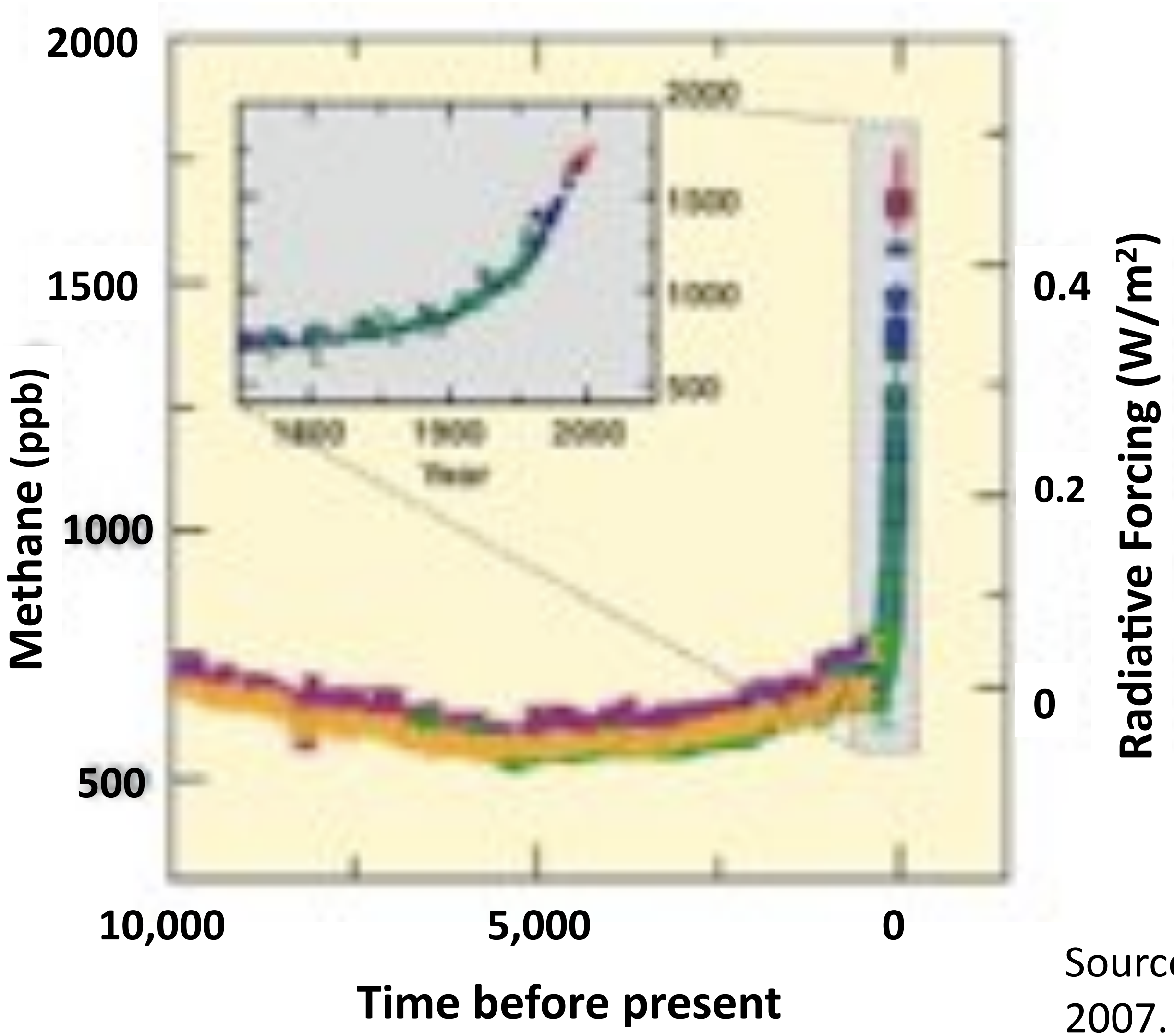
Pre-Industrial cycle spun at 200-250 Tg/yr

Human emissions have short-circuited the cycle, adding 330-380 Tg /yr

1 Tg = 10^{12} grams= 10^6 tonnes = 1 MMT

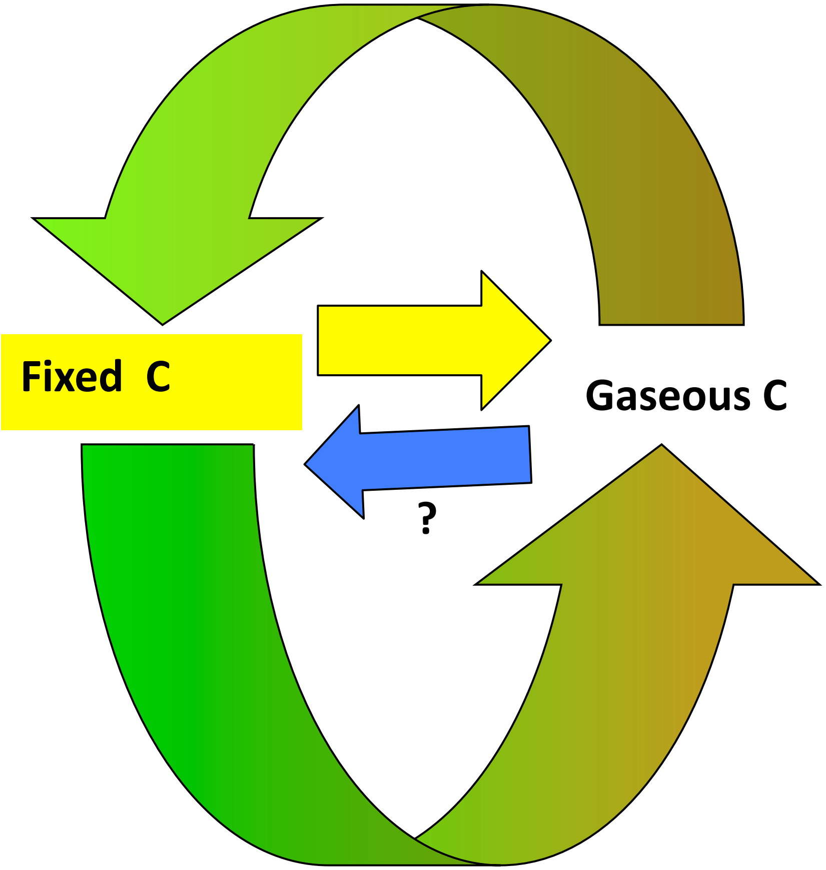
Source: Denman et al., 2007. 4th assessment of the IPCC.

Methane concentrations in the atmosphere are increasing



Source: Denman et al., 2007. 4th assessment of the IPCC.

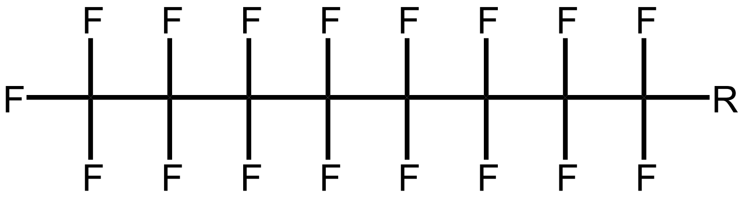
How can we short-circuit the C cycle (in a good way)?



Why not just make lots of non-biodegradable materials?

We’ve done that experiment.

Example: perfluorcarbons (PFCs)



C_4-C_{12}

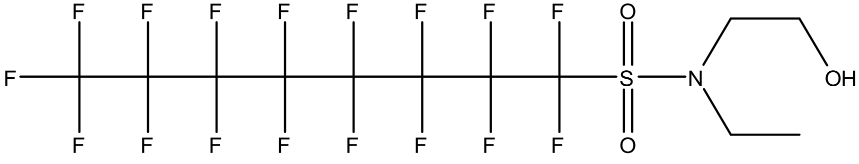
C-F bond
450 kJ/mol

- Stable
- Unique hydrophobic & oleophobic properties
- Applications:
  - Fire-Fighting Foams
  - Wafer Photolithography
  - Insecticides
  - Surfactants
  - Lubricants
  - Coatings
  - Adhesives
  - Stain Repellents ←

The most common stain repellents:

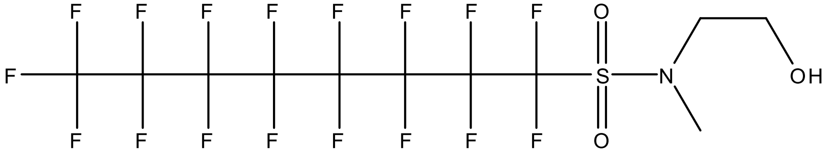
N-EtFOSE

N-ethyl perfluorooctane sulfonamido ethanol



N-MeFOSE

N-methyl perfluorooctane sulfonamido ethanol



PFCs are Everywhere We Look

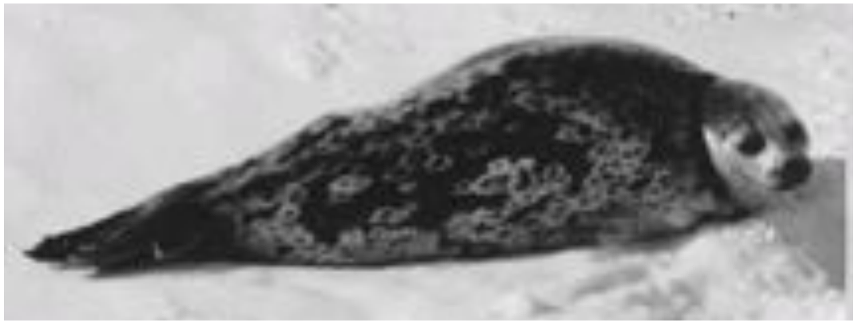
PFOS and PFOA are detected worldwide in waters (red) and animals (yellow), 2007

(adapted from Fujii, 2008)

Even where people are not

4000 ppb in liver

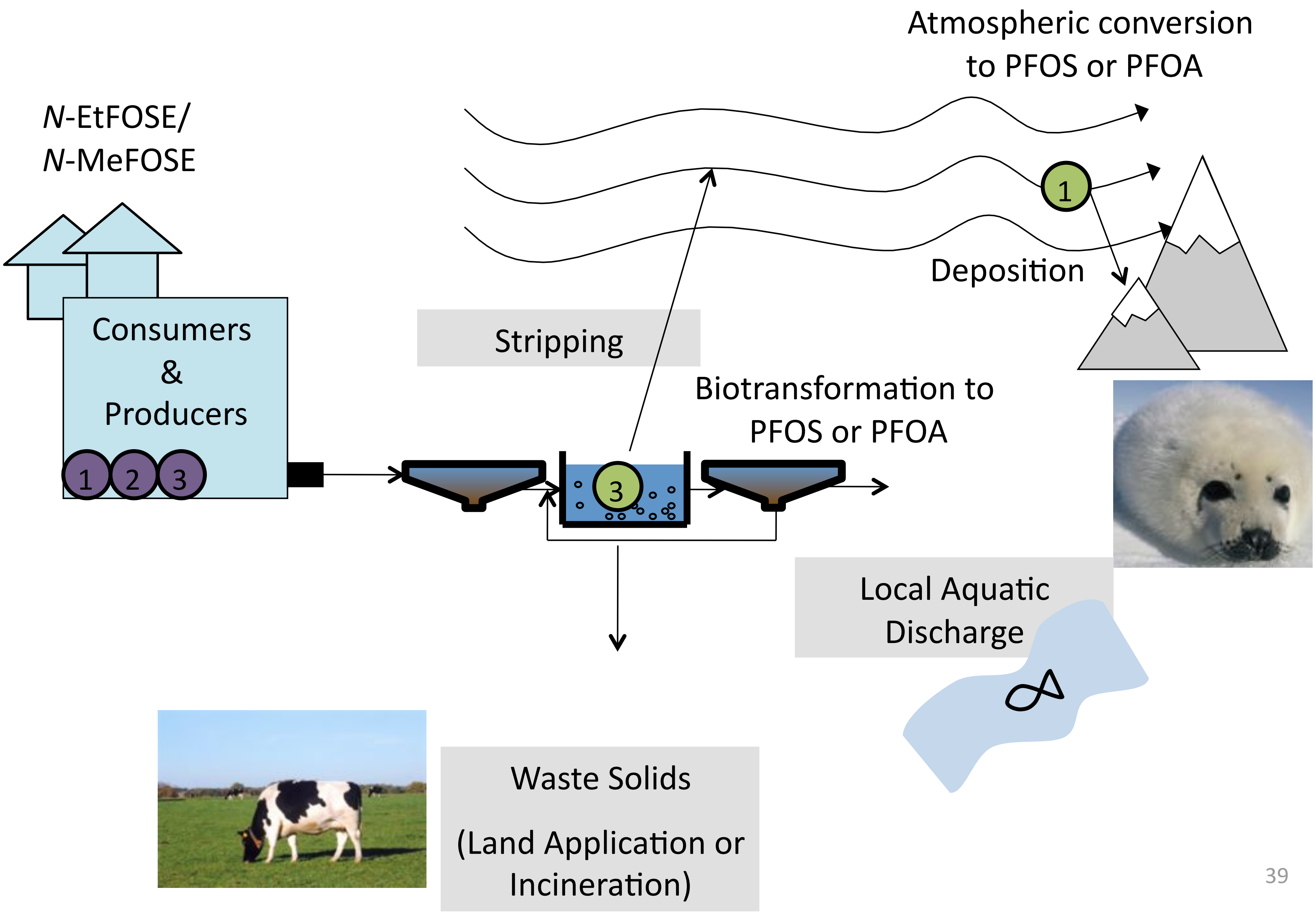
1 ppt in arctic snow



40 ppb in liver

Giesy and Kannan 2001, Young et al. 2007

Where do stain repellants go?



N-EtFOSE/
N-MeFOSE

Consumers
&
Producers

Stripping

Atmospheric conversion
to PFOS or PFOA

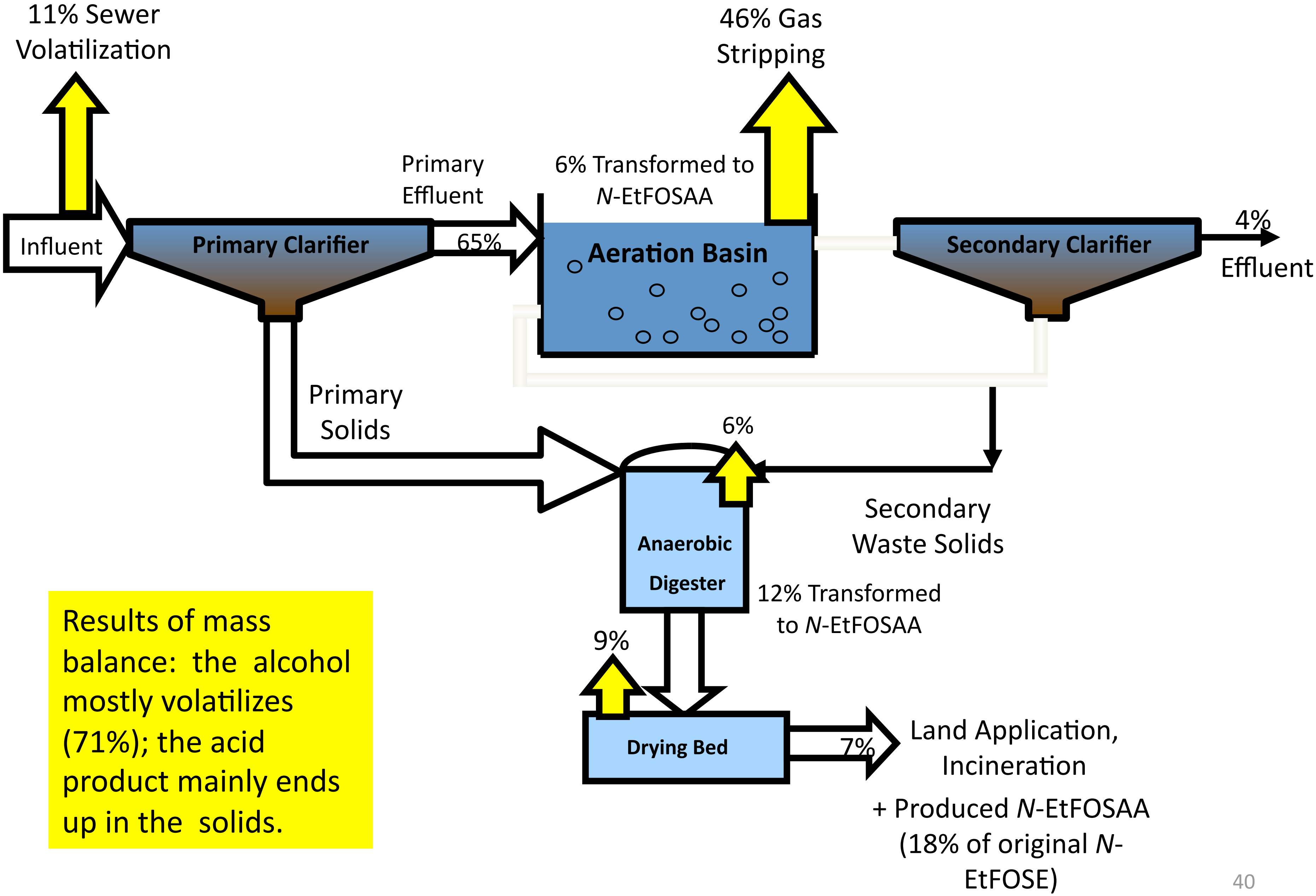
Deposition

Biotransformation to
PFOS or PFOA

Local Aquatic
Discharge

Waste Solids

(Land Application or
Incineration)



11% Sewer Volatilization

Influent

Primary Clarifier

Primary Effluent

65%

6% Transformed to *N*-EtFOSAA

46% Gas Stripping

Aeration Basin

Secondary Clarifier

4%

Effluent

Primary Solids

6%

Secondary Waste Solids

Anaerobic Digester

12% Transformed to *N*-EtFOSAA

9%

Drying Bed

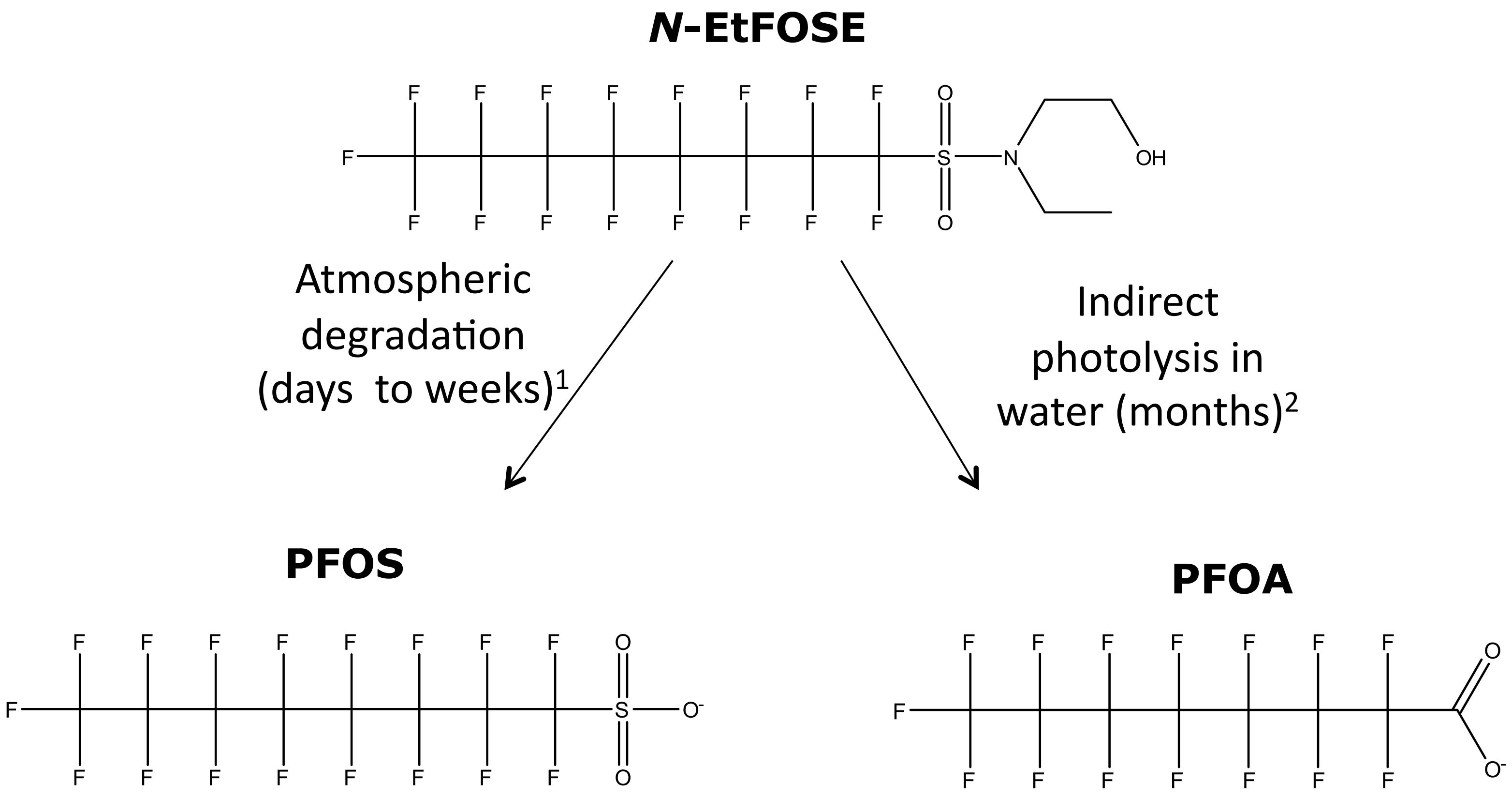
7%

Land Application, Incineration

+ Produced *N*-EtFOSAA (18% of original *N*-EtFOSE)

Results of mass balance: the alcohol mostly volatilizes (71%); the acid product mainly ends up in the solids.

What happens in the air?



***N*-EtFOSE**

Atmospheric degradation (days to weeks)[1]

Indirect photolysis in water (months)[2]

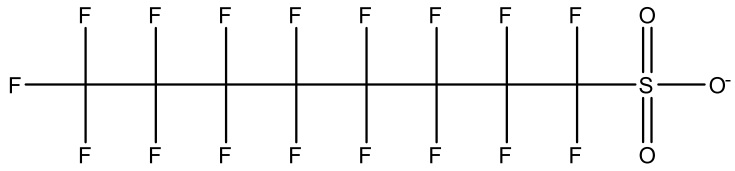
PFOS

PFOA

[1]D'eon 2006 [2]Plumlee 2008

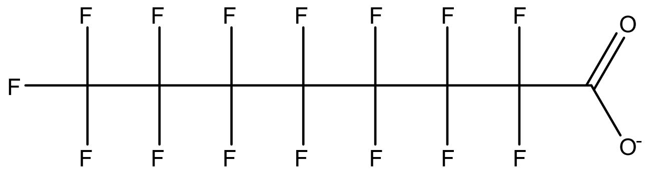
Biological effects & regulations

PFOS



- Monkey death (100%) > 4.5 µg/g-day
- Detected in human blood (~35 ppb)
- US Drinking Water Limit 0.2 ppb

PFOA



- Likely Human Carcinogen
- Detected in human blood (~5 ppb)
- US Drinking Water Limit 0.4 ppb

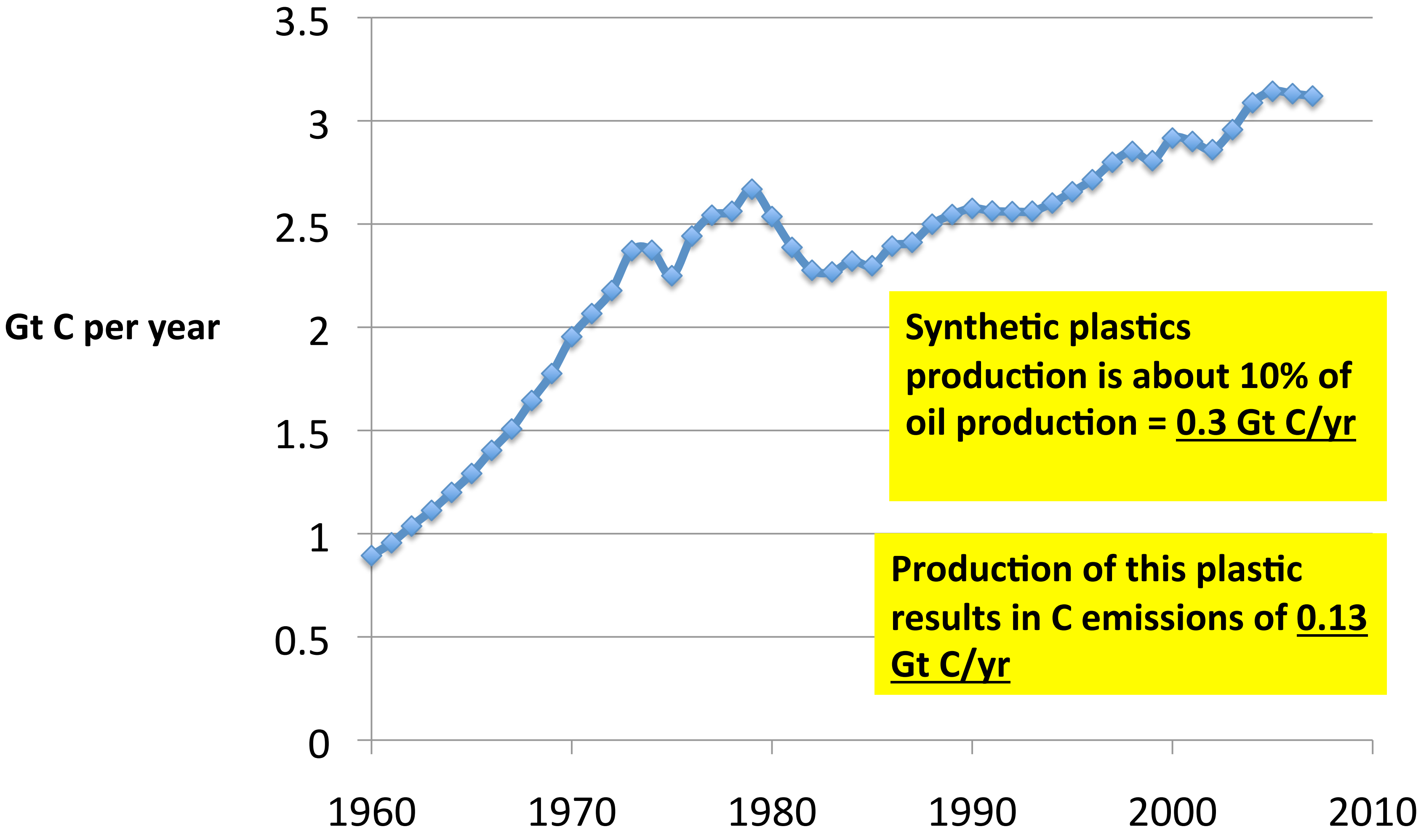
A water reuse application was recently canceled because of PFC concerns (Luthy , 2009)

Another example: **plastics**

- Producing synthetic plastics simply changes the form in which C is sequestered (from fossil fuel to plastic). It does not remove greenhouse gases.

- In fact, because energy is required for production of synthetic plastics, CO_2 is released.

Global Crude Oil Production

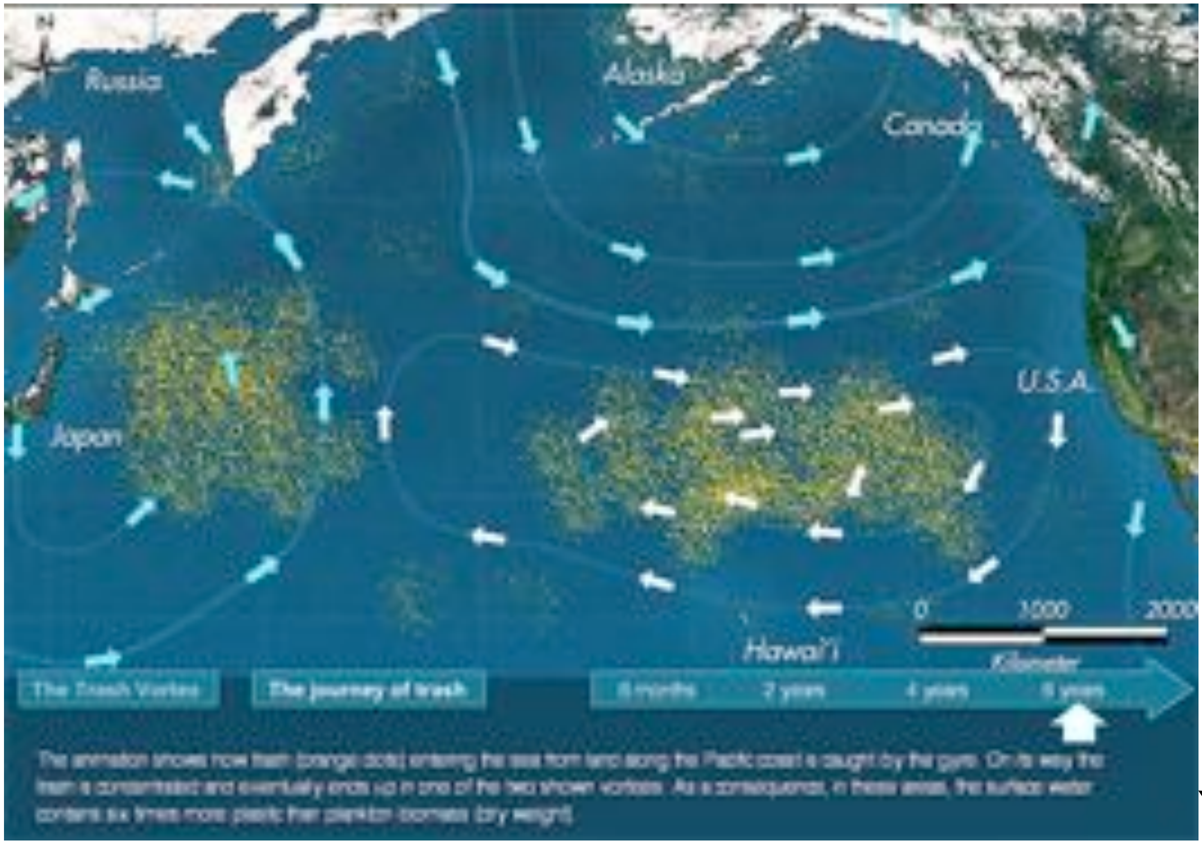


Synthetic plastics production is about 10% of oil production = <u>0.3 Gt C/yr</u>

Production of this plastic results in C emissions of <u>0.13 Gt C/yr</u>

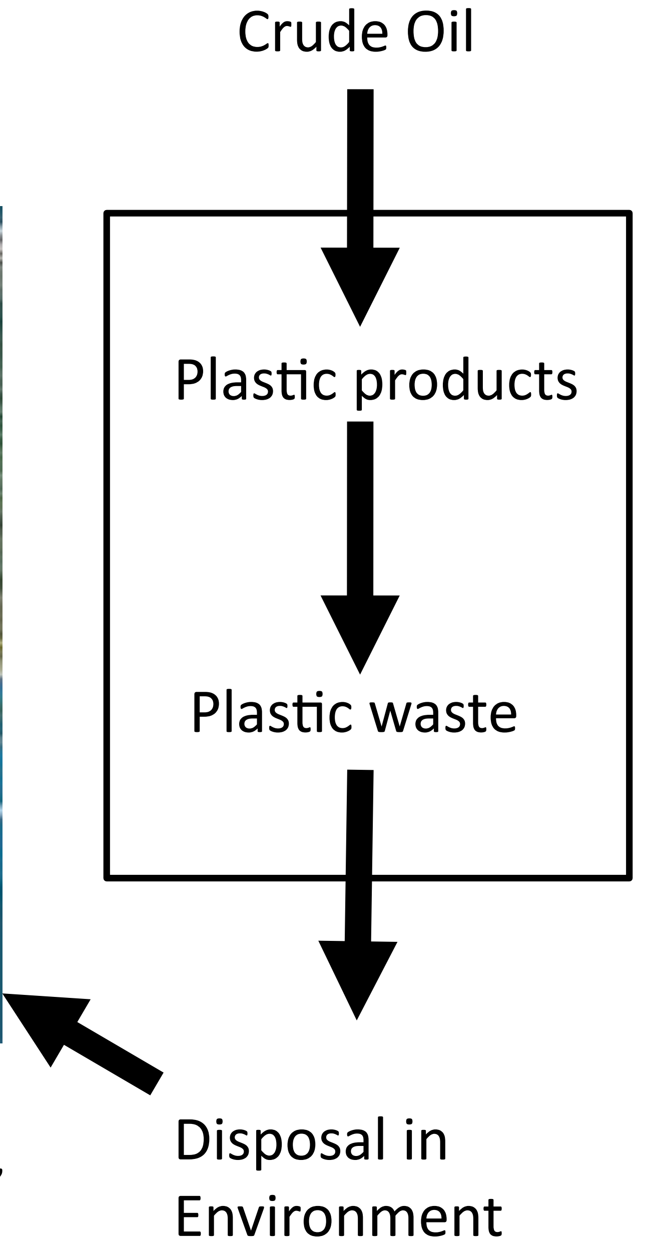
Source of raw data: http://www.eia.doe.gov/aer/txt/ptb1105.html

The linear plastics market leads to unintended adverse consequences



http://community.titantv.com/blogs/lizadeguia/gyre.gif

Synthetic plastics contain potentially harmful additives, such BPA, phthalates, and PBDEs. Toxics adsorbed to plastics, such as DDT, are transported throughout the earth.



Crude Oil

Plastic products

Plastic waste

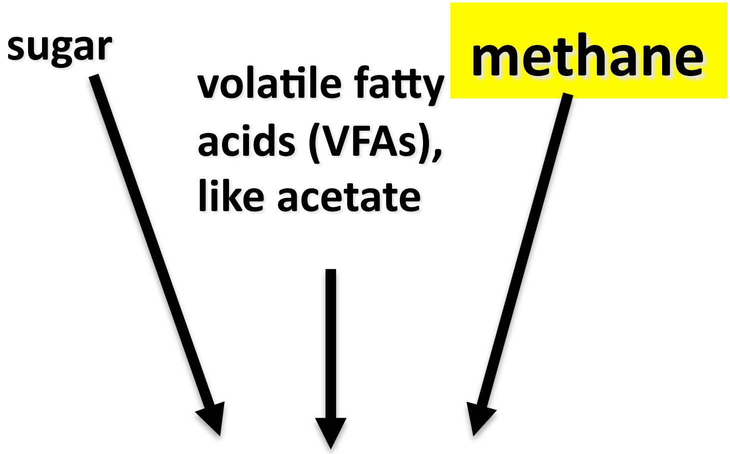
Disposal in Environment

It’s not a cycle

Bioreactors can be used to make ***bioplastics***.

Bioplastics are non-toxic, preventing harm to wildlife and human life. In the marine environment, they break down, preventing long-distance transport of adsorbed pollutants.

Bacteria can make polyhydroxyalkanoate (PHA) bioplastic from a variety of substrates.

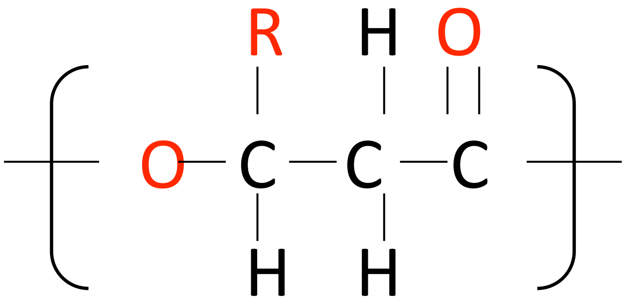


sugar

volatile fatty acids (VFAs), like acetate

methane

Biogas methane is 30-40% less expensive than sugar feedstock

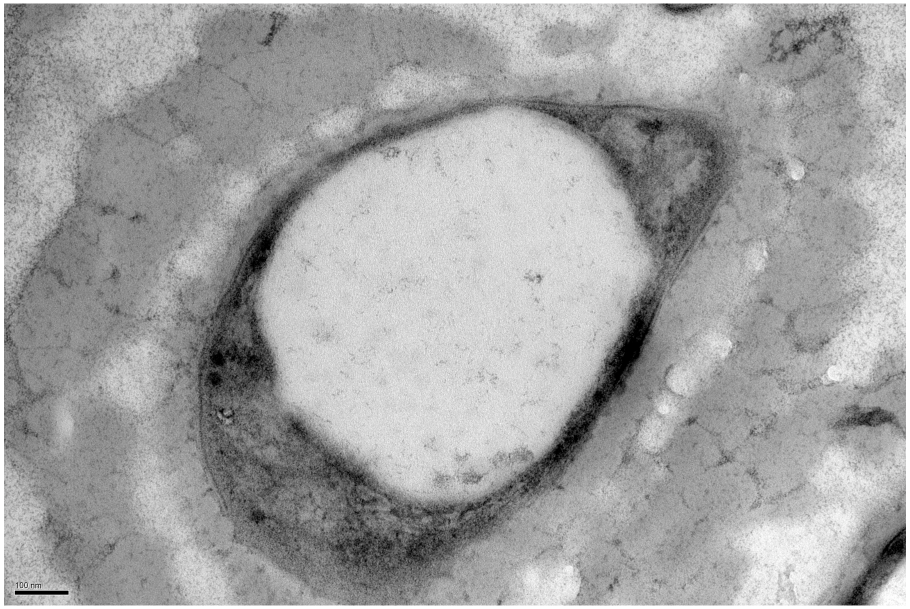


$$\left[-O-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}- \right]$$

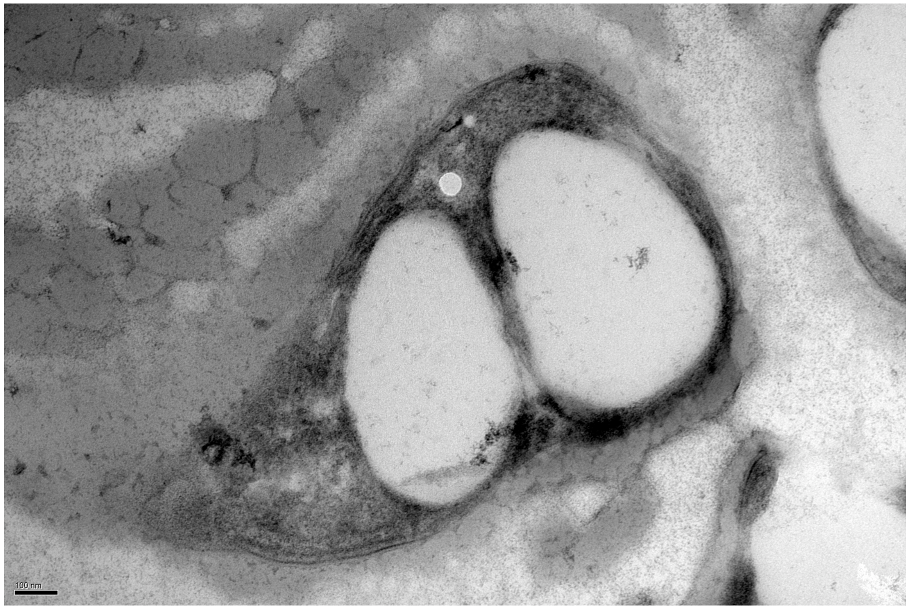
Polyhydroxyalkanoates (PHAs)

When R is a methyl group, the PHA is polyhydroxybutyrate (PHB)

Transmission Electron Microscopy (TEM) imaging
PHB accumulation – 20 hrs

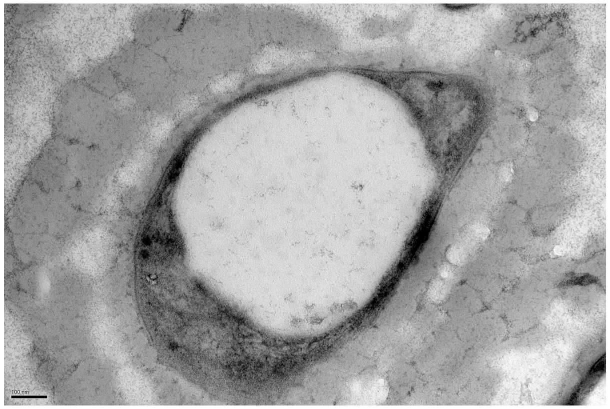


15,000x



12,000x

Processing



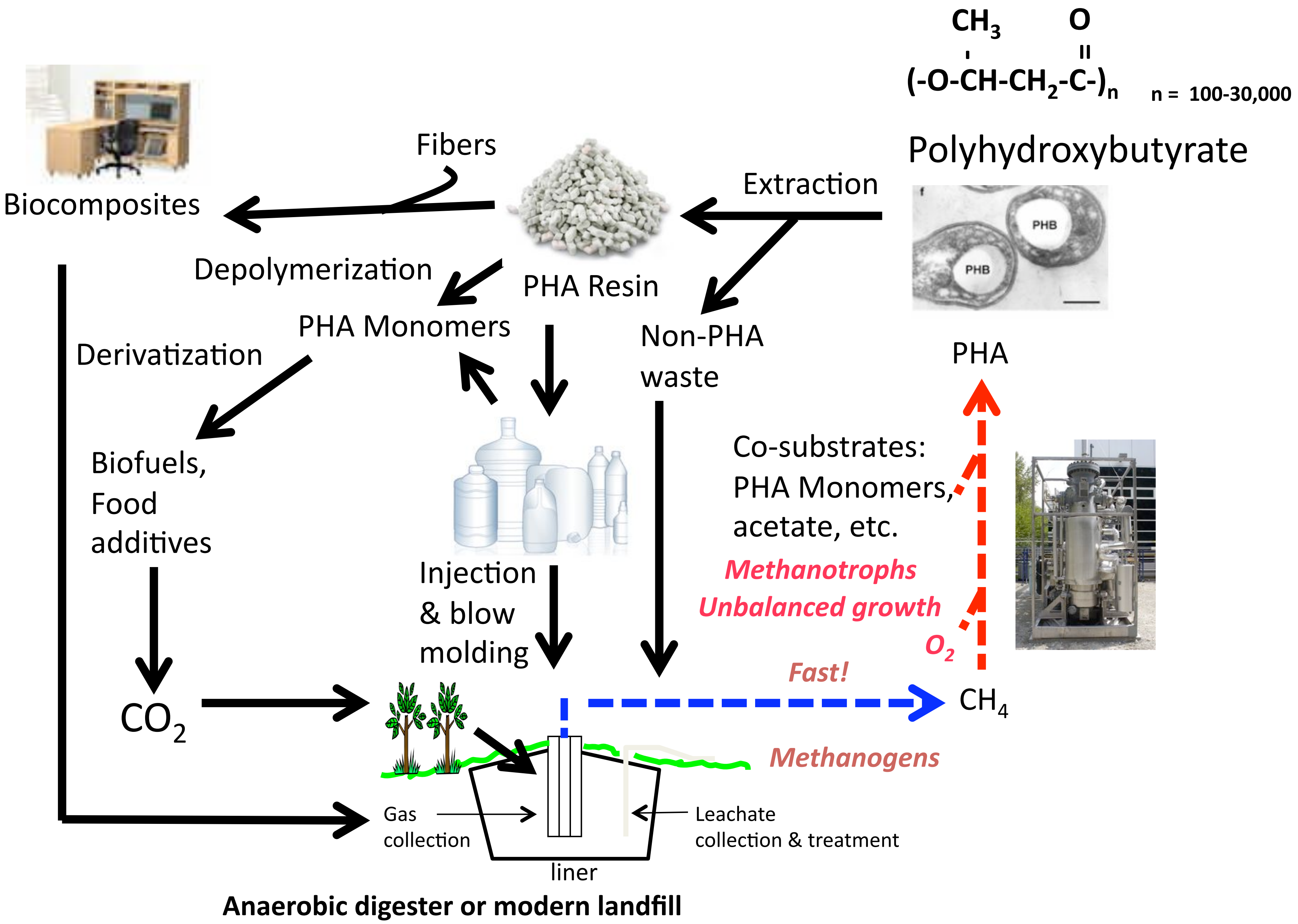
Extraction
Purification
Modification

Extrusion
Injection molding
Blow molding

Challenges remain in the optimization of processing windows and product properties.

http://www.nrc-cnrc.gc.ca/highlights/2007/0703maplesap_e.html
http://www.alternativeconsumer.com/2008/01/18/arrowhead-goes-eco-shape/
http://www.midbury.com/Pile_of_plastic_pellets.gif

The PHA-methane cycle



$$(\text{-O-}\overset{CH_3}{\overset{|}{\text{CH}}}\text{-CH}_2\text{-}\overset{O}{\overset{\|}{\text{C}}}\text{-})_n$$

n = 100-30,000

Polyhydroxybutyrate

Biocomposites

Fibers

Extraction

PHA Resin

Depolymerization

PHA Monomers

Non-PHA waste

Derivatization

Biofuels, Food additives

PHA

Co-substrates: PHA Monomers, acetate, etc.

Methanotrophs

Unbalanced growth

O_2

Injection & blow molding

Fast!

CO_2

CH_4

Methanogens

Gas collection

Leachate collection & treatment

liner

Anaerobic digester or modern landfill

Globally, landfills release about 927 million tonnes of CO_2 equivalents as methane per yr.

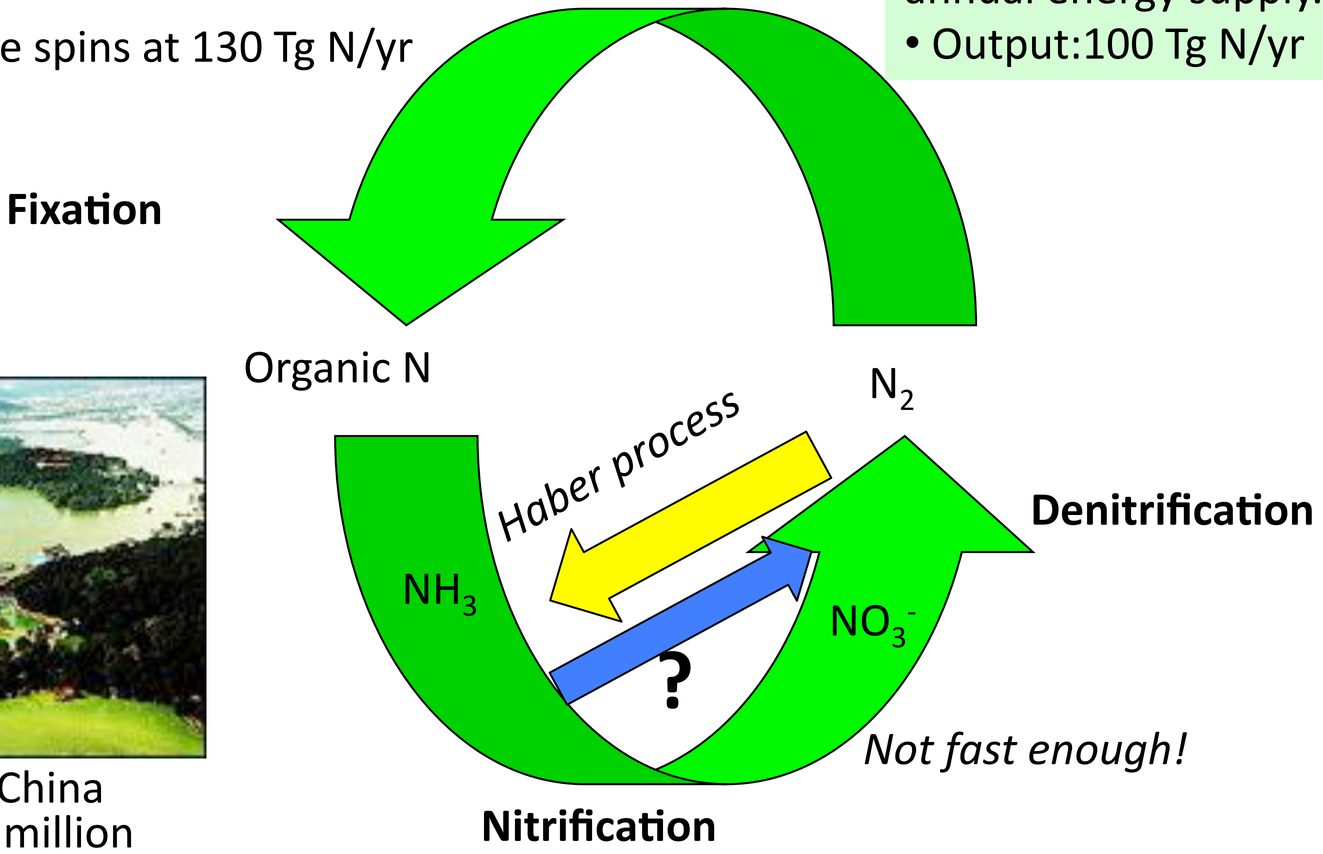
If captured, this methane could theoretically produce ~7 million tonnes of bioplastic per yr.

- **The Nitrogen Cycle**

The Haber Process:
$N_2 + 3H_2 = 2NH_3$

- Input: 1-2% of the world's annual energy supply.
- Output:100 Tg N/yr

Natural cycle spins at 130 Tg N/yr

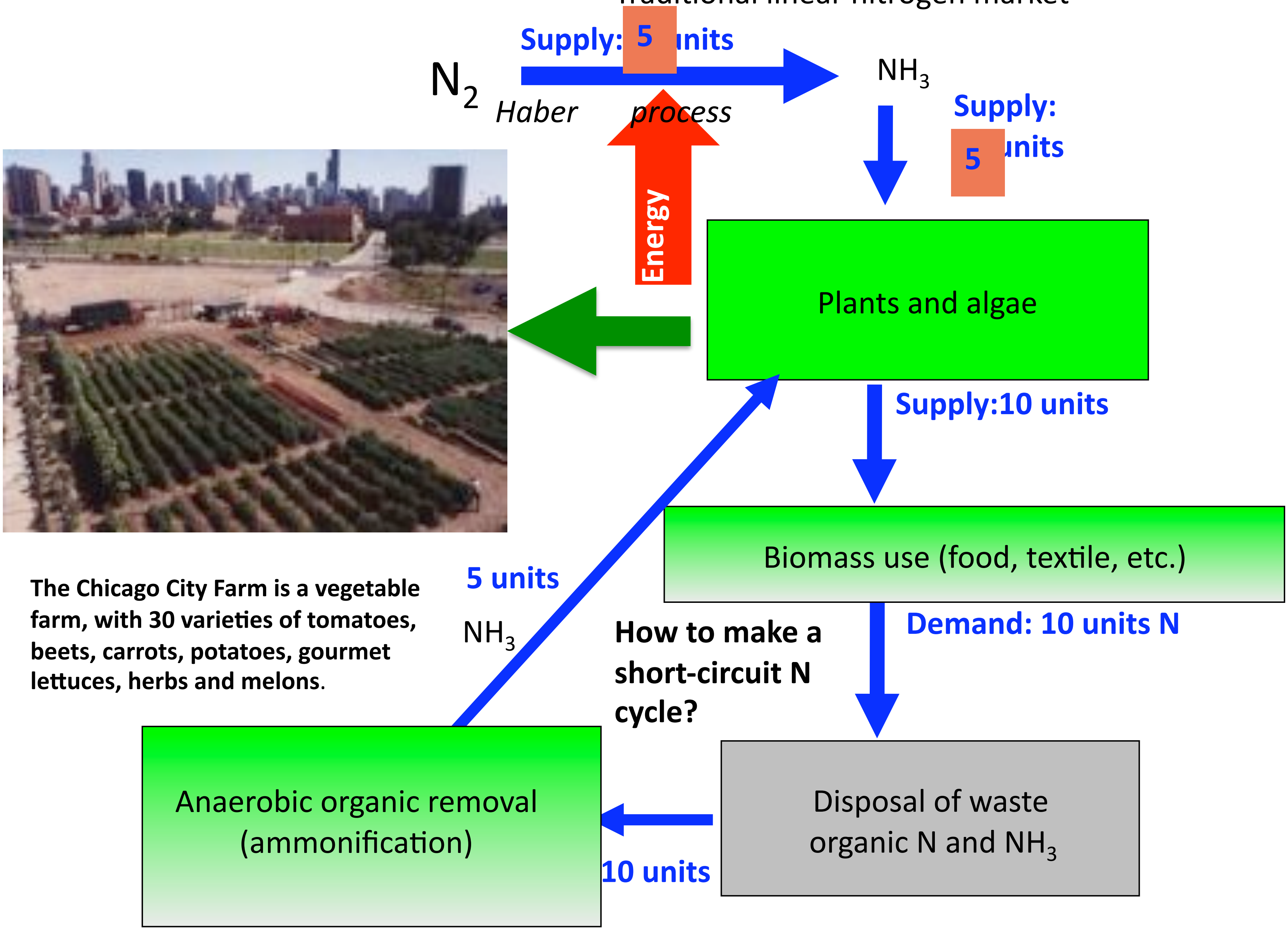


Lake Taihu, China
Supplies 30 million people

1 Tg = 10^{12} grams
10^6 tonnes = 0.001 Gt

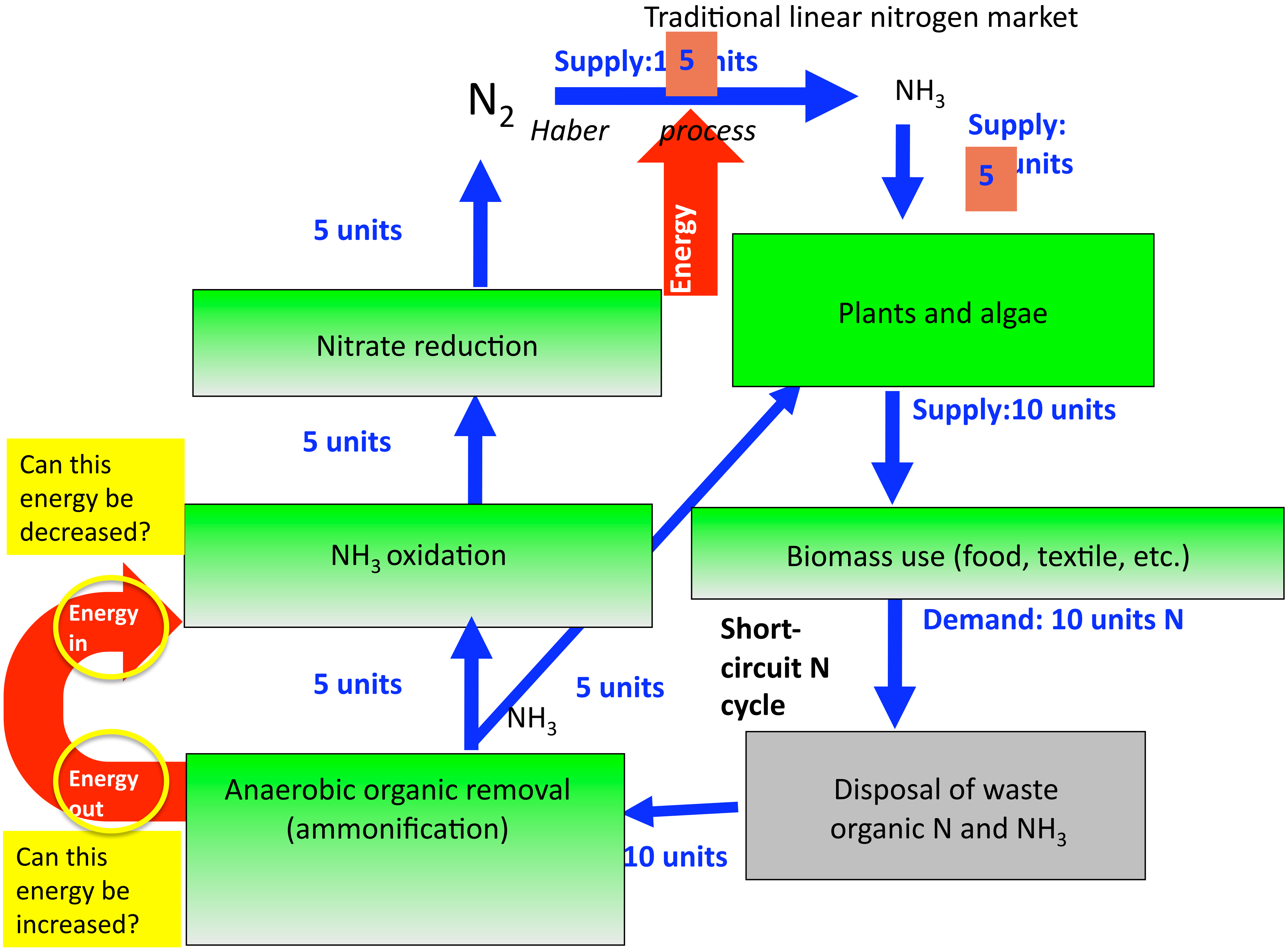
How can we short-circuit the N cycle (in a good way)?

Traditional linear nitrogen market



How to make a short-circuit N cycle?

The Chicago City Farm is a vegetable farm, with 30 varieties of tomatoes, beets, carrots, potatoes, gourmet lettuces, herbs and melons.



Traditional linear nitrogen market

Supply:1 **5** **nits**

N_2 *Haber process* NH_3

Energy

Supply:
5 **units**

5 units

Nitrate reduction

Plants and algae

Supply:10 units

5 units

Can this
energy be
decreased?

NH_3 oxidation

Biomass use (food, textile, etc.)

Energy in

Demand: 10 units N

Short-circuit N cycle

5 units

NH_3

5 units

Energy out

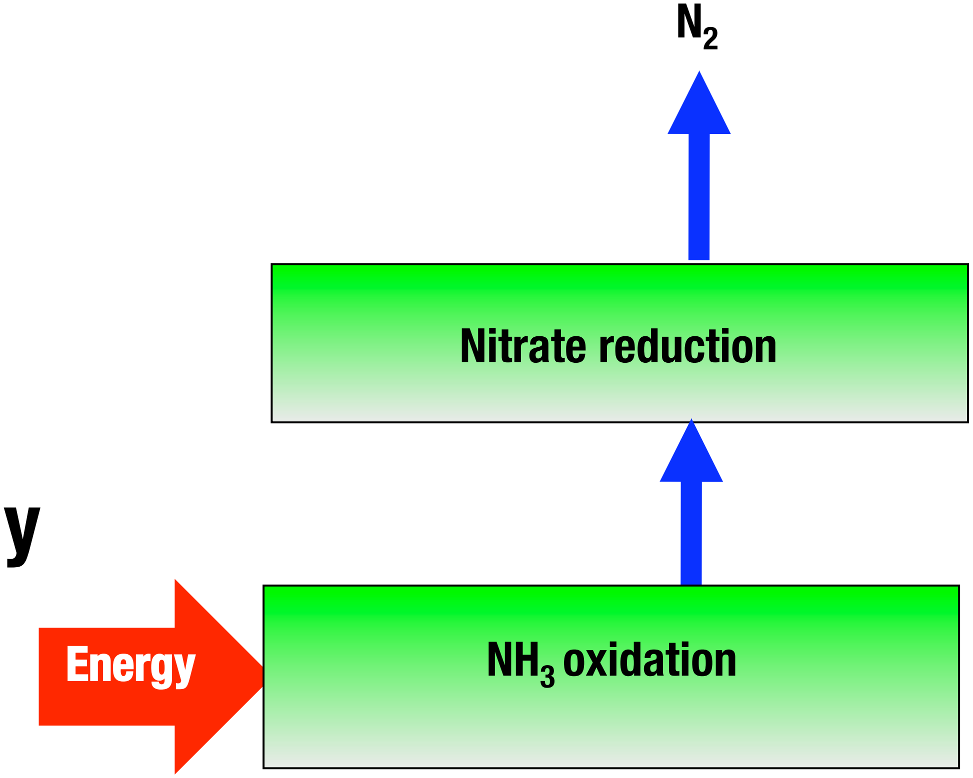
Anaerobic organic removal
(ammonification)

Disposal of waste
organic N and NH_3

10 units

Can this
energy be
increased?

Can this energy input be decreased?



N_2

Nitrate reduction

Energy

NH_3 oxidation

<u>YES</u>! By managing bioreactor communities to “short-circuit” the N cycle, it is *theoretically* possible that a future bioreactor will treat domestic wastewater using 60% less O_2 and producing 3 times more methane than current bioreactors.

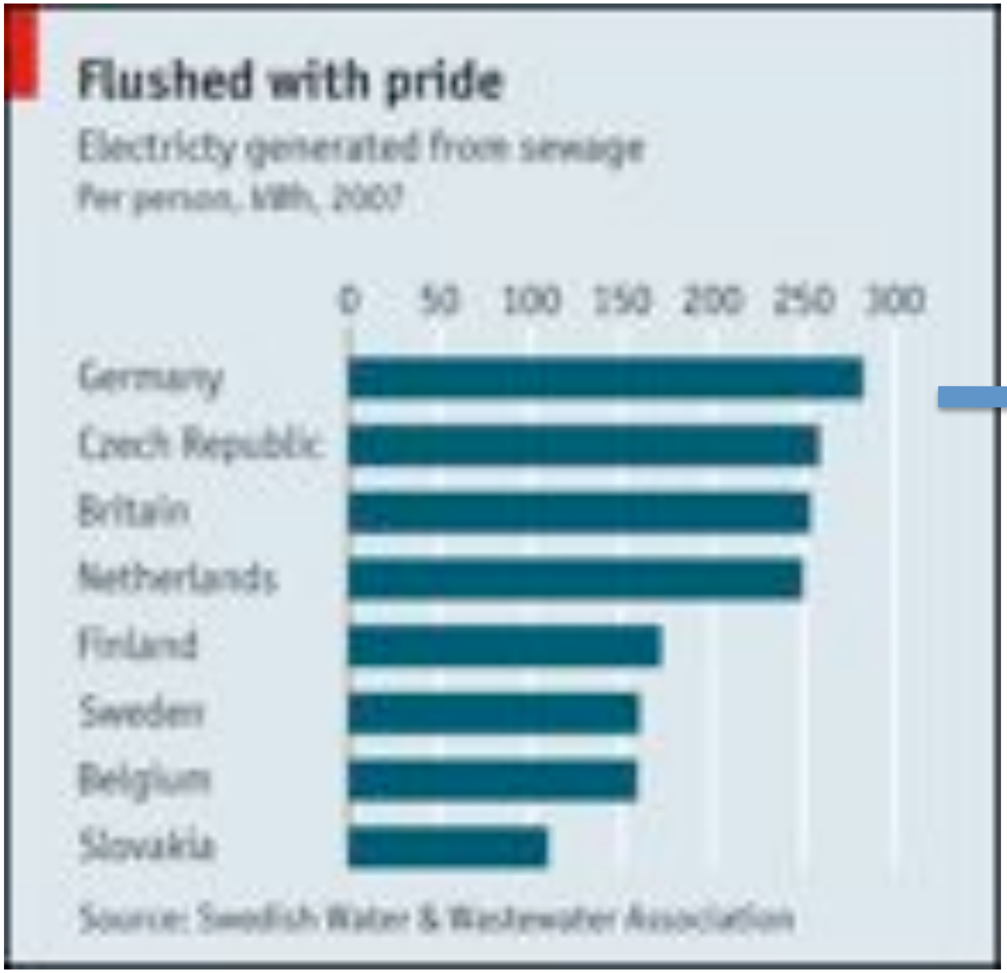
The key is microbial ecology.

How much methane could *theoretically* be obtained from one liter of domestic wastewater with N removal as N_2?

Assumptions: typical sewage with 300 mg BOD_L/L and 40 mg N/L
N removal as N_2, C removal as CH_4.

1st stage C removal	2nd stage N removal	mg O_2/L	ml CH_4 (STP)/L
Aerobic (anaerobic digestion of primary solids)	Traditional N cycle Nitrification - Denitrification	186	30
Direct anaerobic treatment	Traditional N cycle Nitrification – Denitrification	183	35
	Short-circuit N cycle: Sharon process	137	59
	Short-circuit N cycle: Sharon + Anammox	69	93

Europe currently leads in energy recovery from wastewater



Flushed with pride

Electricity generated from sewage

Per person, kWh, 2007

Source: Swedish Water & Wastewater Association

The Economist, 2 January 2010

~ $30/person-yr. For an average household of 3 people, ~$90/mo.

Average household uses about 900 kWh/month, or about 90 x 12 = $1080/yr.

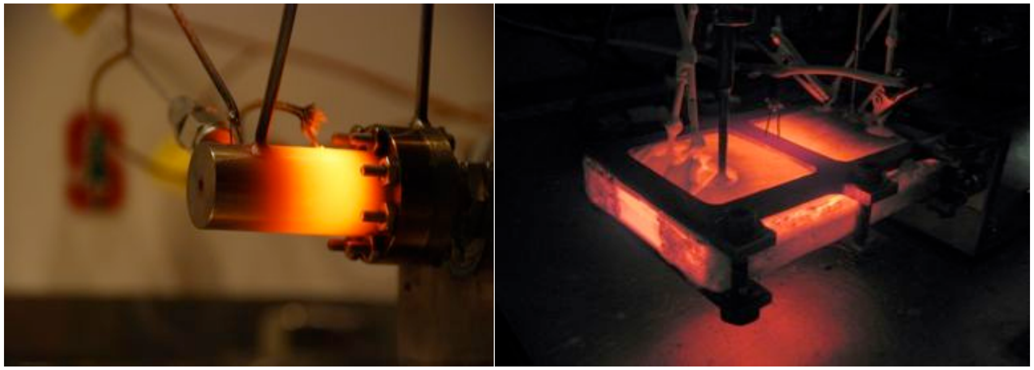
The German electricity production decreases household cost by ~9%.

ammonia removal and energy production

$2NH_3 + 2O_2 \text{ -> } N_2O + 3H_20$

$N_2O \text{ -> } N_2 + 0.5O_2 + 82\ \text{kJ}$

Net: $2NH_3 + 2O_2 \text{ -> } N_2 + 0.5O_2 + 3H_2O + 82\ \text{kJ}$



N_2O decomposition cell
Scherson and Cantwell (2008)

CANDO: Short-circuit nitrification with catalytic N_2O decomposition

BOD_L reducing power savings: (5-0)/5x100=100%

Reducing power for denitrification:
0 moles e-/mol N

O_2 saving
(2-0.75)/

O_2 for nitrification:
1-0.25 =0.75 moles O_2 per mol N oxidized

$0.5N_2 + 0.25\ O_2$

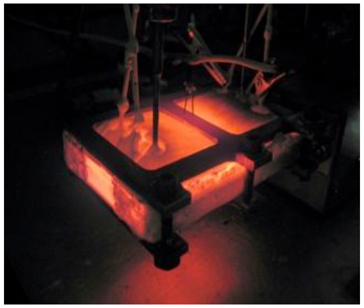
+ 41 kJ

$0.5N_2O$

AOB and AOA

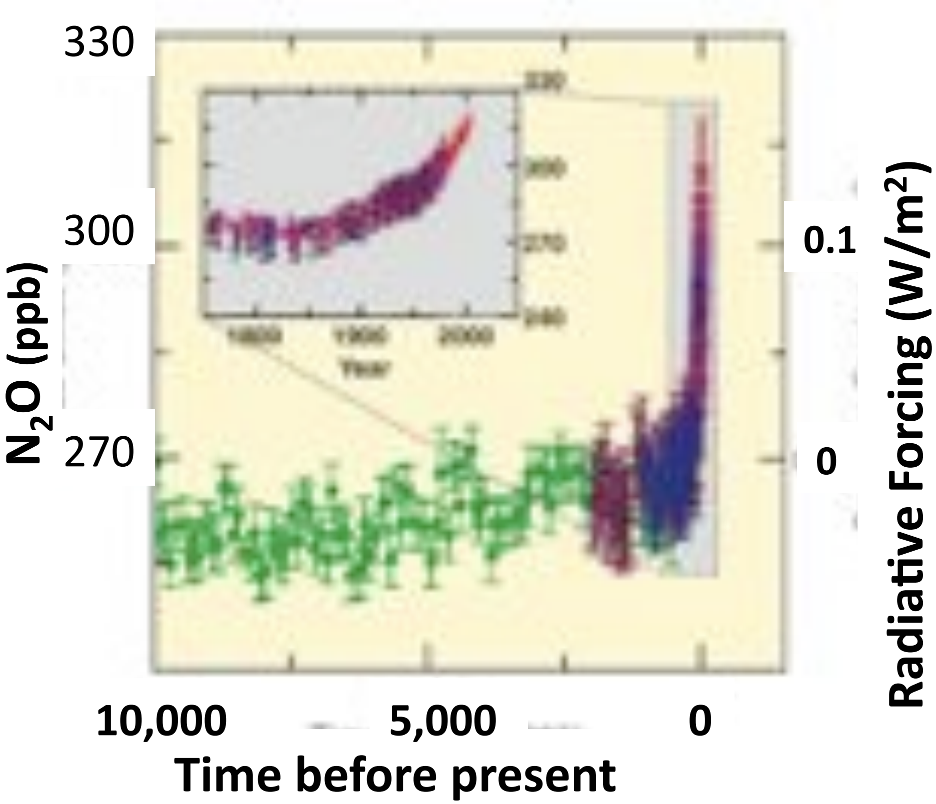
$1.0\ O_2$

NH_3



N_2O decomposition cell
(Scherson and Cantwell, 2008)

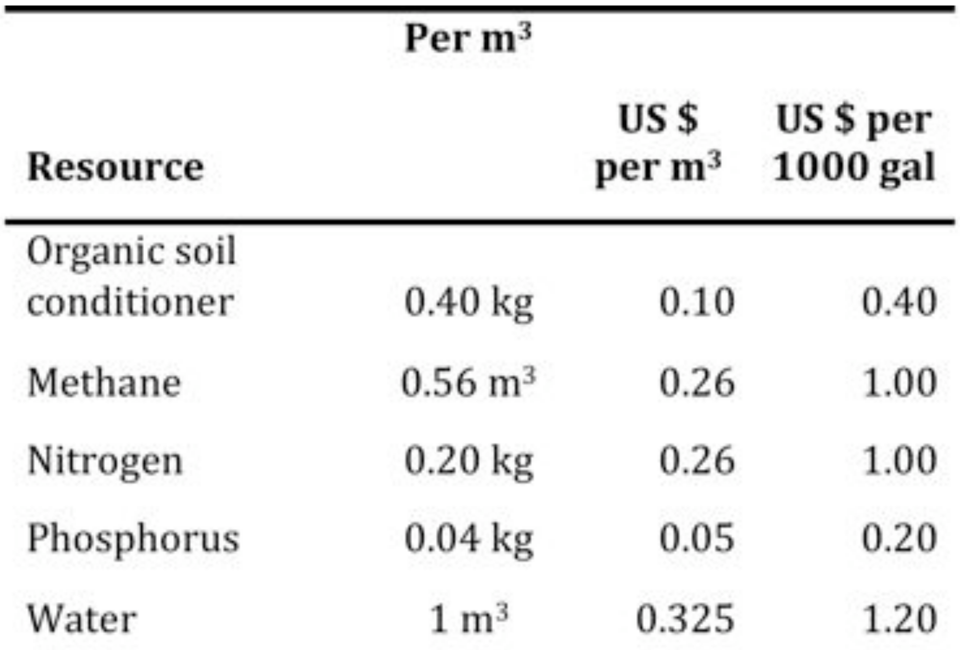
Decomposition of N_2O also eliminates a serious greenhouse gas



N_2O is 298 X more powerful as a global warming agent than CO_2 over a 100 year period.

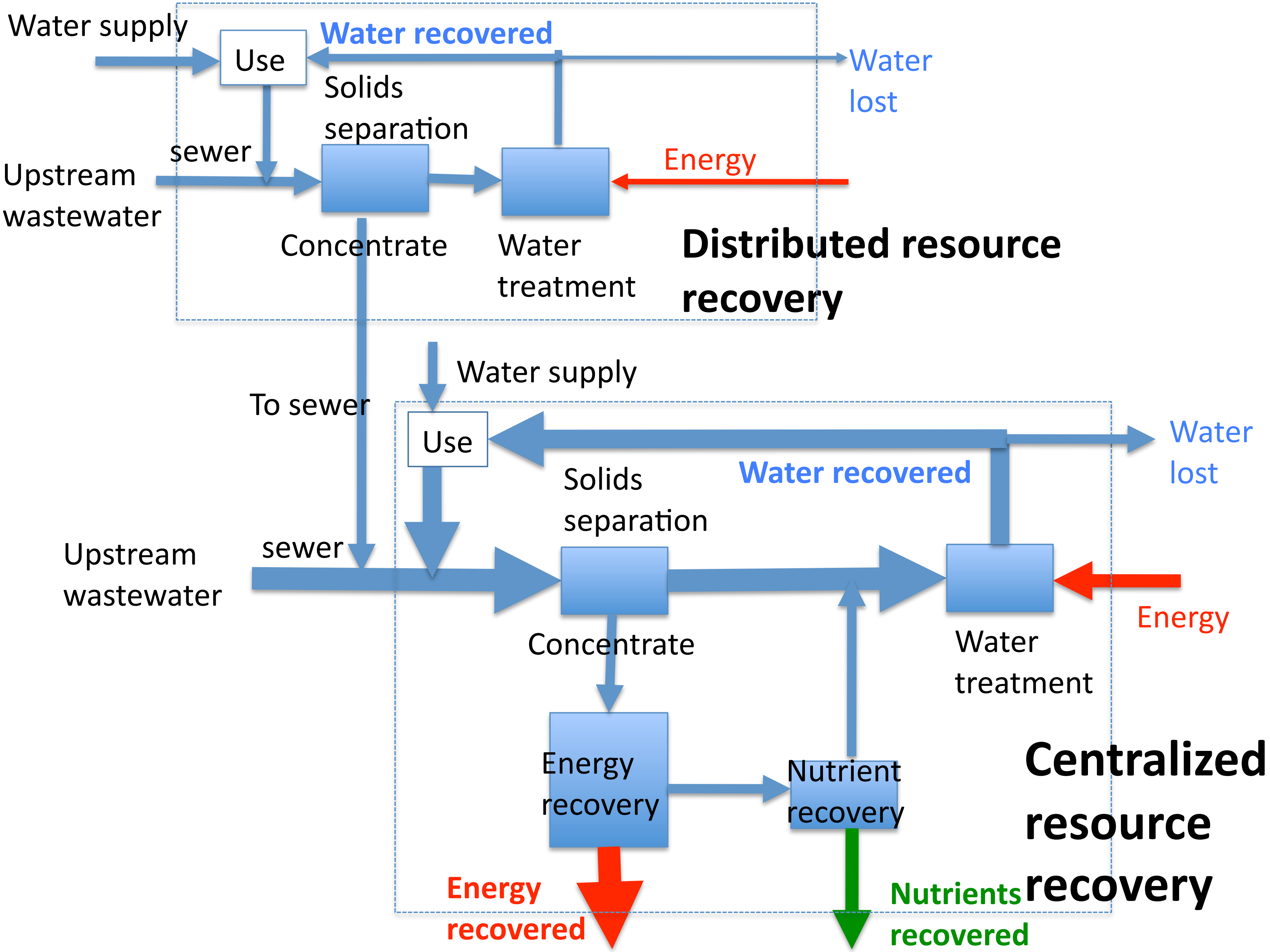
Source: Denman et al., 2007. 4th assessment of the IPCC.

The value of wastewater resources at centralized facilities if 75% of the water is removed by scalping.



Resource	Per m^3	US \$ per m^3	US \$ per 1000 gal
Organic soil conditioner	0.40 kg	0.10	0.40
Methane	0.56 m^3	0.26	1.00
Nitrogen	0.20 kg	0.26	1.00
Phosphorus	0.04 kg	0.05	0.20
Water	1 m^3	0.325	1.20

Removal of three quarters of the water quadruples the value of the organics and nutrients in one m^3 of wastewater. Now the energy and nutrient value is equivalent to the value of the water.



Water supply

Use

Water recovered

Water lost

Solids separation

sewer

Upstream wastewater

Energy

Concentrate

Water treatment

Distributed resource recovery

To sewer

Water supply

Use

Water lost

Solids separation

Water recovered

Upstream wastewater

sewer

Energy

Concentrate

Water treatment

Energy recovery

Nutrient recovery

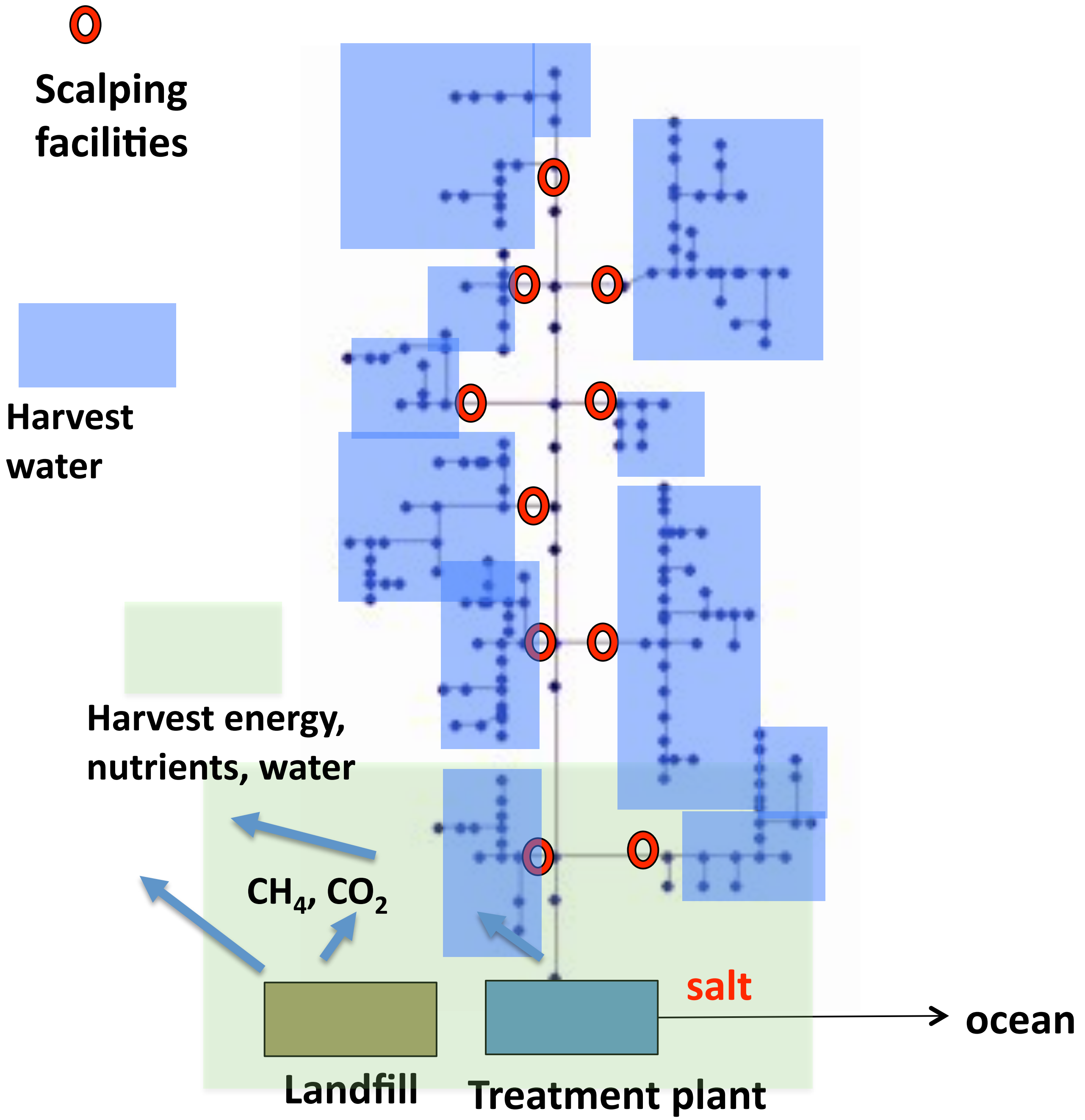
Centralized resource recovery

Energy recovered

Nutrients recovered

New strategies for resource recovery

We are currently developing water and energy balances for the service area of the City of Palo Alto



Scalping facilities

Harvest water

Harvest energy, nutrients, water

CH_4, CO_2

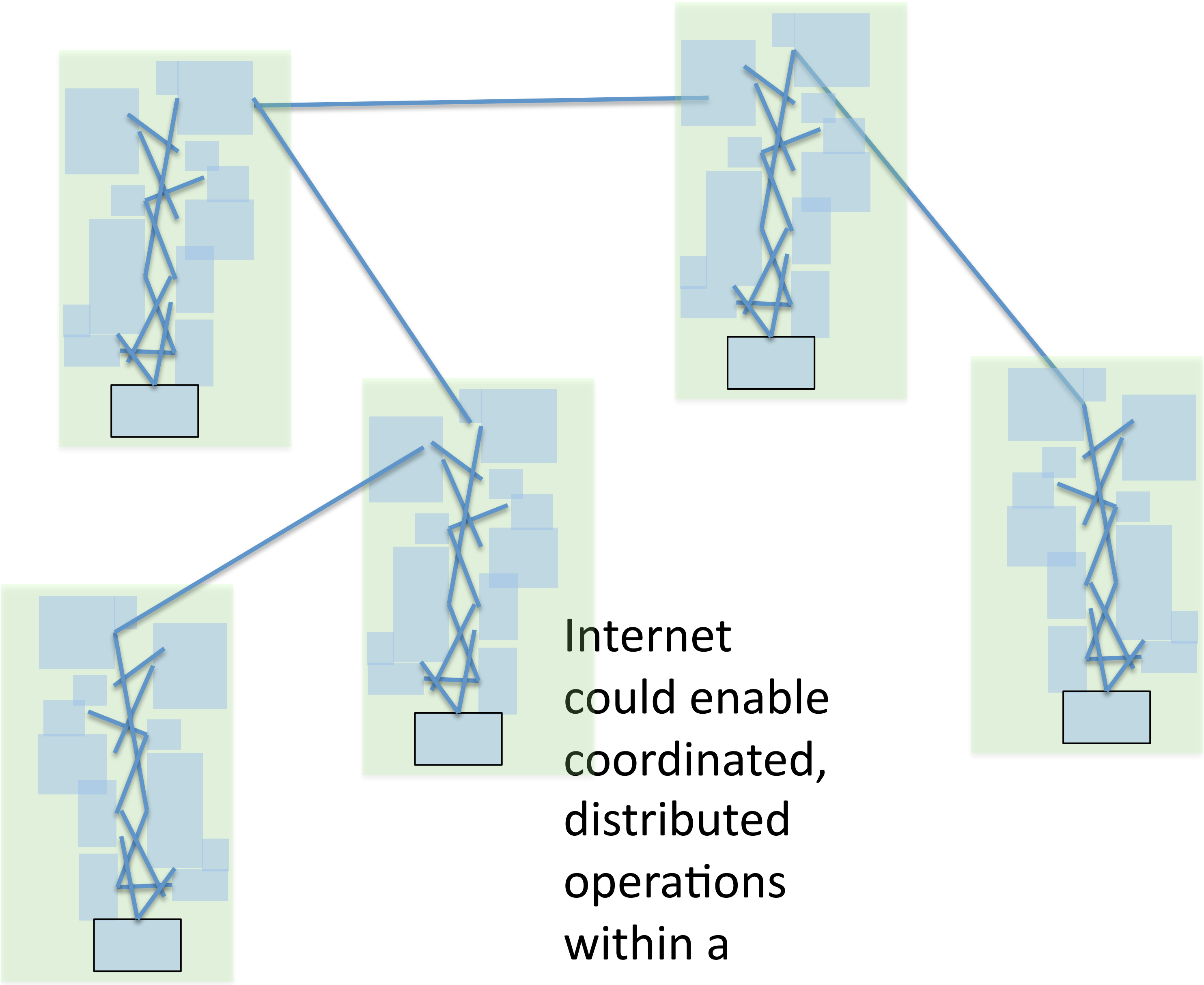
salt

ocean

Landfill

Treatment plant

and between adjacent service areas



Internet
could enable
coordinated,
distributed
operations
within a
service area

New bioreactors; new systems

- *Efficient removal of trace toxic organics & pathogens*.
- *Efficient recovery of energy, material, nutrients*
- *Simple, distributed operation*
- *Low O_2 consumption and low biomass solids production*
- *Greenhouse gas control*

Support

Woods Institute for the Environment, Stanford University

Palo Alto Regional Water Quality Control Plant

U.S. National Science Foundation

California EPA