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CEE 370 Environmental Engineering Principles

Lecture #23
Water Quality Management I: Pollutants and Sources

Reading: Mihelcic & Zimmerman, Chapter 7
Davis & Cornwall, Chapt 5-1 to 5-2
Davis & Masten, Chapter 9-1 to 9-2

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Question

- What is the biggest water quality problem in rivers and lakes today?
  A. Dissolved oxygen
  B. Pathogens
  C. Endocrine disrupters
  D. Cyanotoxins
  E. Organic solvents

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Water Quality

- Measures of Water Quality
  - DO and Oxygen Demand
  - Solids
  - Nutrients
  - Metals
  - Pathogens
  - Organic compounds
    - Toxics
    - Bioactive compounds
- Sources and Quantities
- Water Quality Modeling

Introduction

Water Pollution:

The presence of any harmful chemical or other constituent present in concentrations above the naturally occurring background level.

Wastewater:

discarded or previously used water from a municipality or industry

Waste Sources

- Point Sources
  - Municipal Wastewater
  - Industrial Wastewater
  - Tributaries
- Non-point sources
  - agricultural
  - silvicultural
  - atmospheric
  - urban & suburban runoff
  - groundwater

Well defined origin
easily measured
more constant

Diffuse origin
more transient
often dependent on precipitation

Treatment is generally feasible

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Typical Municipal WW Charact.

Parameter	Typical Wastewater Characteristics, mg/L except pH	U.S. EPA Discharge Standards, mg/L except pH	Typical Concentrations in Lakes or Streams, mg/L except pH
BOD_5	150-300	30	2-10
Total Suspended Solids	150-300	30	2-20
COD	400-600	N/A	5-50
D.O.	0	4-5	4-Sat.
NH_3-N	15-40	*	<1
NO_3	0	*	<1
pH	6-8	6-9	6-8

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Pathogenic Organisms

- Viruses
  - Polio, Norfolk agent, Hepatitis
- Bacteria
  - Typhoid, Cholera, Shigella, Salmonella
  - Antibiotic resistant forms
- Protozoans
  - Cryptosporidium, Giardia

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Dissolved Oxygen (D.O.)

- Oxygen is a rather insoluble gas
  - often the limiting constituent in the aerobic purification of wastes and natural waters
  - solubility ranges from 14.6 mg/L at 0°C to about 7 mg/L at 35°C.
    - In addition to temperature, its solubility varies with barometric pressure and salinity.
  - The saturation concentration of oxygen in distilled water may be calculated from Henry's law

M&Z Equ #7.11

$$DO_{sat} = K_H p_{O_2}$$

KH=	1.36E-03	
PO2=	0.21	
DOsat=	2.86E-04	M
GFW=	32	
DOsat=	9.14	mg/L

$$K_H = 1.36x10^{-3} \frac{moles}{L-atm}$$ at 20°C

  - But if you need to adjust to other temperaturs, the following empirical expression is more useful:

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DO saturation formula

$$C_s = C_{sl} P \left\{ \frac{\left[1 - \left(\frac{P_{wv}}{P} \right)\right](1 - \theta P)}{(1 - P_{wv})(1 - \theta)} \right\}$$

where:

P_{vw} = water vapor partial pressure (atm)
= 11.8571 - (3840.70/T_k) + (216,961/T_k^2)

P = total atmospheric (barometric) pressure (atm), which may be read directly or calculated from a remote reading at the same time from:
= P_o - (0.02667)ΔH/760

ΔH = Difference in elevation from the location of interest (at P) to the reference location (at P_o) in feet.

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DO (cont.)

P_o = Simultaneous barometric pressure at a nearby reference location

θ = pressure/temperature interactive term
= 0.000975 - (1.426x10^{-5}T) + (6.436x$10^{-8}$$T^2$)

T = Temperature in degrees centigrade

C_{s1} = Saturation concentration of oxygen in distilled water at 1 atmosphere total pressure.

ln(C_{s1}) = -139.34411 + (1.575701x10^5/T_k) - (6.642308x10^7/T_k^2) + (1.243800x10^{10}/T_k^3) - (8.621949x10^{11}/T_k^4).

T_k = Temperature in degrees Kelvin (T_k = T + 273.15)

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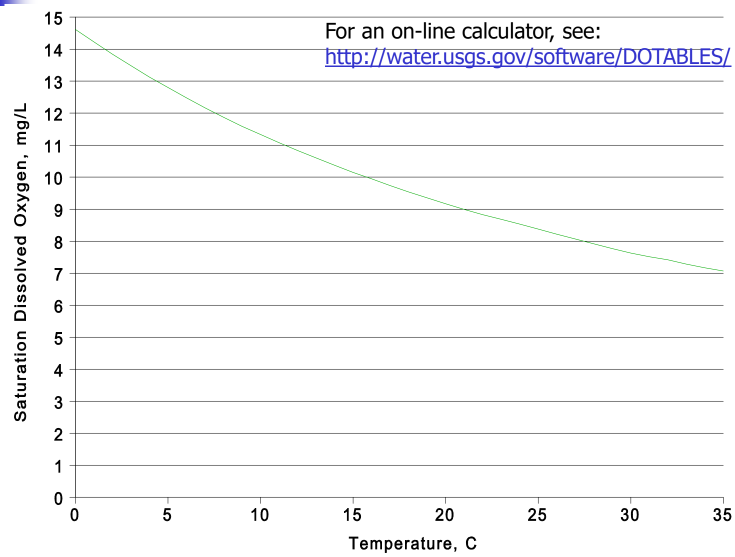
DO Saturation Profile



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DO (cont.)

- Minimum concentration is required for the survival of higher aquatic life
  - larval stages of certain cold-water fishes are quite sensitive
- Significant discharges of organic wastes may depress the D.O. concentrations in receiving waters
  - microbially-mediated oxidation
  - each state has established ambient dissolved oxygen standards
- Another use of D.O. is the assessment of oxidation state in groundwaters and sediments

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DO (cont.)

- also a very important parameter in biological treatment processes
  - indicates when aerobic and anaerobic organisms will predominate
  - used to assess the adequacy of oxygen transfer systems
  - indicates the suitability for the growth of such sensitive organisms such as the nitrifying bacteria.
- used in the assessment of the strength of a wastewater through either the Biochemical Oxygen Demand (BOD) or respirometric studies.

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Insufficient DO

Solutions – Reduce DO "demand"

- reduction of BOD by biological WW treatment
- nutrient control

Ambient Water Quality Criteria

- established by EPA in **"Gold Book"**
- dependent on type of fish, averaging period

Ambient Water Quality Standards [enforceable]

- established by states, and other local agencies
- dependent on use classification

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Oxygen Demand

- It is a measure of the amount of "reduced" organic and inorganic matter in a water
- Relates to oxygen consumption in a river or lake as a result of a pollution discharge
- Measured in several ways
  - BOD - Biochemical Oxygen Demand
  - COD - Chemical Oxygen Demand
  - ThOD - Theoretical Oxygen Demand

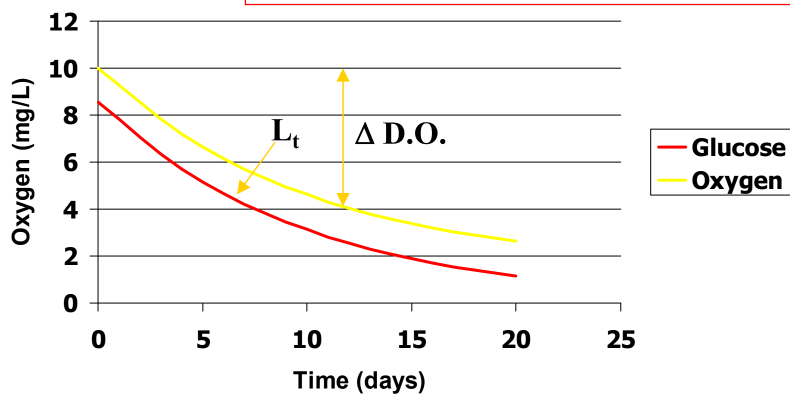
BOD: A Bioassay

Briefly, the BOD test employs a bacterial seed to catalyze the oxidation of 300 mL of full-strength or diluted wastewater. The strength of the un-diluted wastewater is then determined from the dilution factor and the difference between the initial D.O. and the final D.O.

$$BOD_t \equiv DO_i - DO_f$$

Glucose example

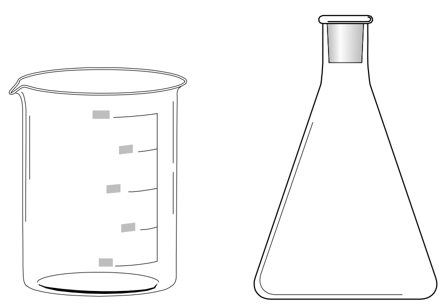
$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$



BOD with dilution

When BOD>8mg/L

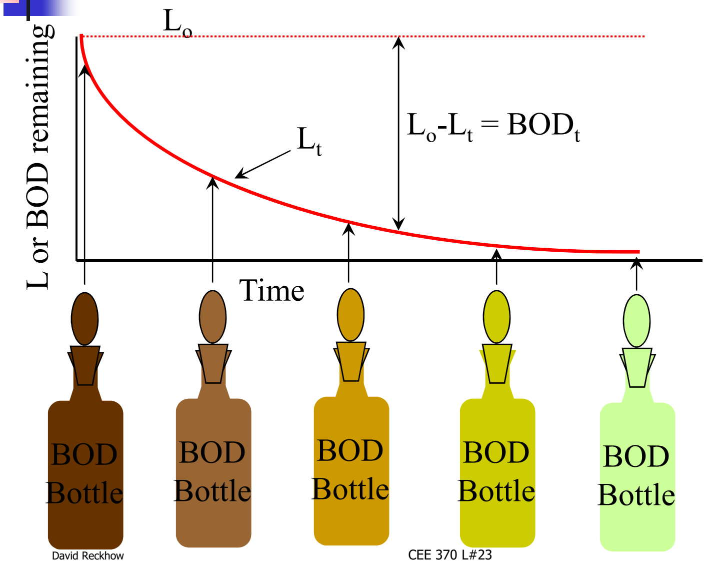
$$BOD_t = \frac{DO_i - DO_f}{\left(\frac{V_s}{V_b}\right)}$$



Where

- BOD_t = biochemical oxygen demand at t days, [mg/L]
- DO_i = initial dissolved oxygen in the sample bottle, [mg/L]
- DO_f = final dissolved oxygen in the sample bottle, [mg/L]
- V_b = sample bottle volume, usually 300 mL, [mL]
- V_s = sample volume, [mL]

BOD - loss of biodegradable organic matter (oxygen demand)



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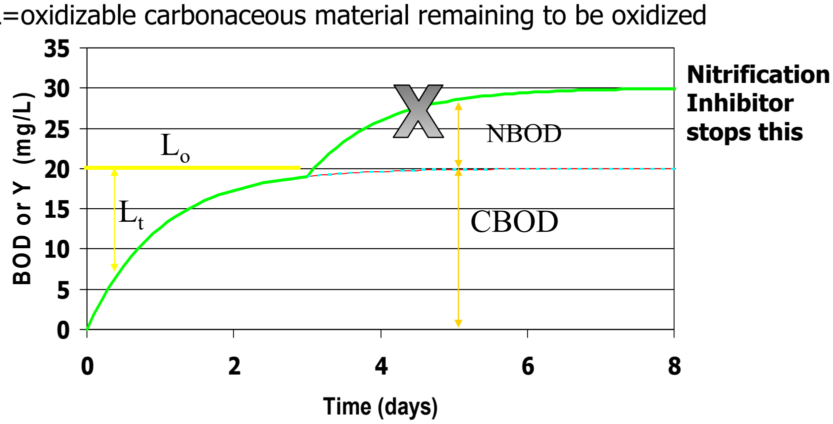
The BOD bottle curve

- L=oxidizable carbonaceous material remaining to be oxidized



$$BOD_t \equiv y_t = L_o - L_t$$

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BOD Modeling in a BOD test

"L" is modelled as a simple 1st order decay: $\frac{dL}{dt} = -k_1 L$

Which leads to: $L = L_o e^{-k_1 t}$

And combining with: $BOD_t \equiv y_t = L_o - L_t$

We get: $BOD_t \equiv y_t = L_o(1 - e^{-k_1 t})$

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Temperature Effects

Temperature Dependence

- Chemist's Approach: Arrhenius Equation

$$\frac{d(\ln k)}{dT_a} = \frac{E_a}{RT_a^2}$$

$$k_{T_a} = k_{293^o K} e^{E_a (T_a - 293)/RT_a 293}$$

- Engineer's Approach:

$$k_T = k_{20^o C} \theta^{T - 20^o C}$$

For CBOD
Often we use: θ=1.047
D&M cite: 1.056 for 20-30C
and 1.135 for 4-20C

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NBOD

Nitrogeneous BOD (NBOD)

$$NH_3 + 1.5O_2 \xrightarrow{Nitrosomonas} NO_2^- + H_2O + H^+$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{Nitrobacter} NO_3^-$$

2 moles oxygen/1 mole of ammonia
4.57 grams oxygen/gram ammonia-nitrogen

Like CBOD, the NBOD can be modelled as a simple 1st order decay:

$$\frac{dL^N}{dt} = -k_N L^N$$

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NBOD cont.

- The model is then:

$$NBOD_t = L_o^N\left(1 - e^{-k_N t}\right)$$

  - where:

$$L_o^N \equiv NBOD_u = 4.57(org - N + NH_3 - N)$$

- Nitrifiers
  - very slow generation time (~1 day)
  - sensitive to low D.O.
- NBOD may be very important for non-nitrified, but otherwise highly treated waters

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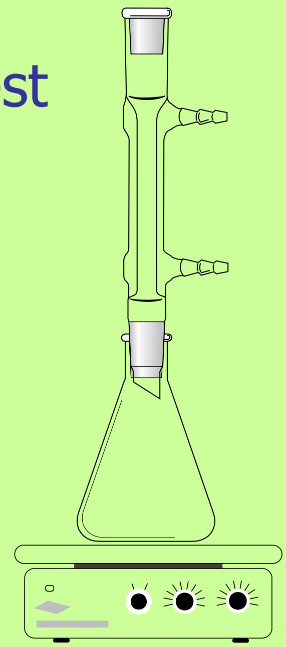
COD: A chemical test

The chemical oxygen demand (COD) of a waste is measured in terms of the amount of potassium dichromate ($K_2Cr_2O_7$) reduced by the sample during 2 hr of reflux in a medium of boiling, 50% H_2SO_4 and in the presence of a Ag_2SO_4 catalyst.



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COD (cont.)

The stoichiometry of the reaction between dichromate and organic matter is:

$$C_nH_aO_b + \Psi Cr_2O_7^{-2} + 8\Psi H^+ \rightarrow nCO_2 + 2\Psi Cr^{=3} + \left(4\Psi + \frac{a}{2}\right)H_2O$$

Where: $$\Psi = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3}$$

- COD test is faster than BOD analysis: used for quick assessment of wastewater strength and treatment performance
- Like the BOD, it does not measure oxidant demand due to nitrogeneous species
- It does not distinguish between biodegradable and non-biodegradable organic matter. As a result COD's are always higher than BOD's.

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ThOD

- This is the total amount of oxygen required to completely oxidize a known compound to CO_2 and H_2O. It is a theoretical calculation that depends on simple stoichiometric principles. It can only be calculated on compounds of known composition.
- We've done these calculations already

Organic Content

- TOC: total organic carbon
  - measured with a TOC analyzer
  - related to oxygen demand, but does not reflect the oxidation state of the organic matter
- other group parameters
  - oil & grease
- specific organic compounds

TOC

Total organic carbon analysis is a determination of organic carbon in a sample regardless of its oxidation state or biodegradability. Other measures of total organic matter (e.g., COD, BOD) may respond differently to solutions of equal carbon concentration depending on the oxygen content or the bidegradation kinetics. For the measurement of total organic carbon, the sample is exposed to an oxidizing environment often at very high temperatures. With complete oxidation all carbon is converted to carbon dioxide and swept into a detector by the carrier gas. The oxidation process is based on the following stoichiometry:

$$C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$

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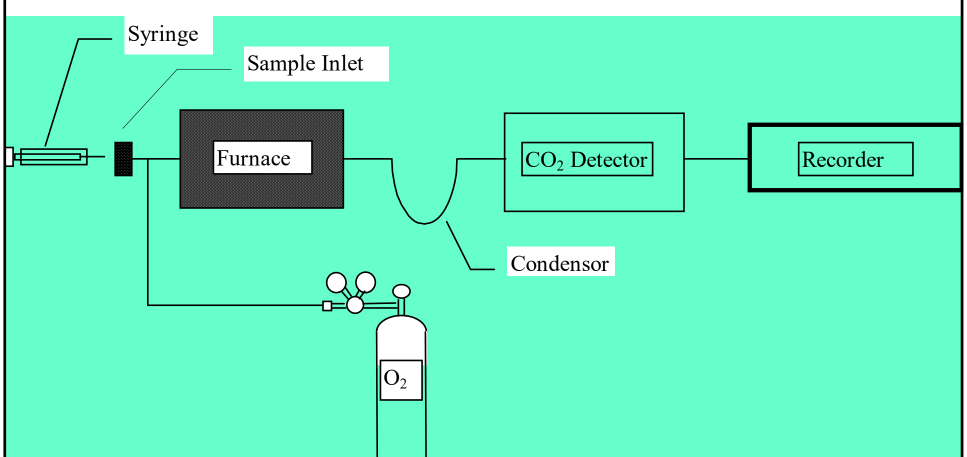
TOC - Pyrolysis Instrument



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Filter

NOM Quantification: TOC & DOC

Principle: oxidize all organic matter to Carbon dioxide and water. Then measure the amount of carbon dioxide produced

$$C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$

Oxidation

- High Temperature Pyrolysis
- UV Irradiation
- Heated Persulfate
- UV/Persulfate

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Organic Carbon Fractions

- Total Carbon (TC)
  - Inorganic Carbon (IC)
    - Purgeable (Dissolved)
    - Non-Purgeable (Particulate)
  - Total Organic Carbon (TOC)
    - Purgeable Organic Carbon (POC)
    - Non-purgeable Organic Carbon (NPOC)
      - Particulate (PtOC)
      - Dissolved (DOC)

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Solids: significance

- TDS: Total Dissolved Solids
  - used as a measure of "salinity"
    - Indicates when water is unsuitable for drinking or agricultural use
- TSS: Total Suspended Solids
  - Measure of "muddiness" of a water
    - used to assess clarifier performance
- VSS: Volatile Suspended Solids
  - Used to estimate bacterial populations in wastewater treatment systems

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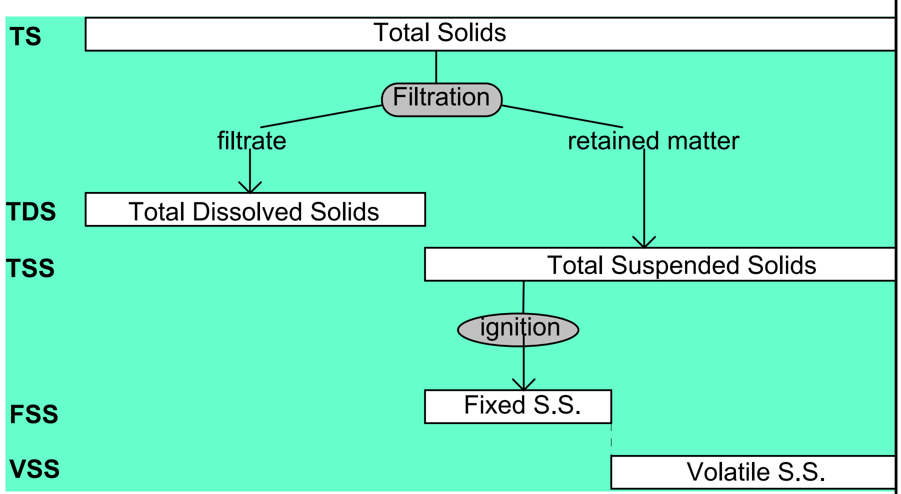
Solids Analysis



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Particle Analysis

Example 2.15 & 2.16, on pg. 30-31 of Mihelcic

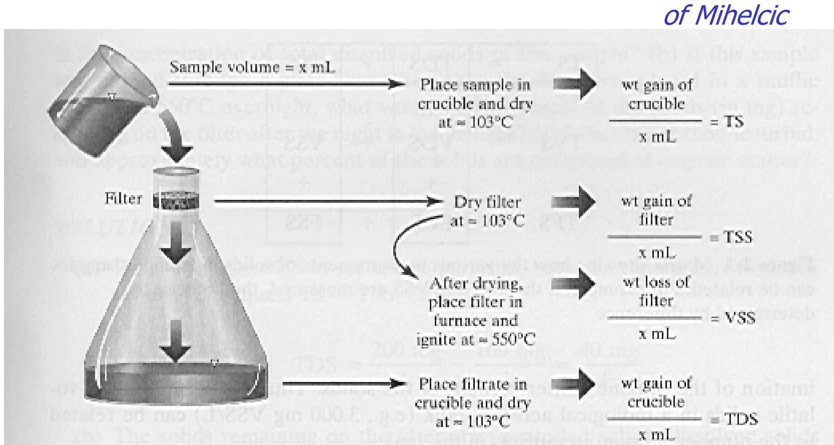
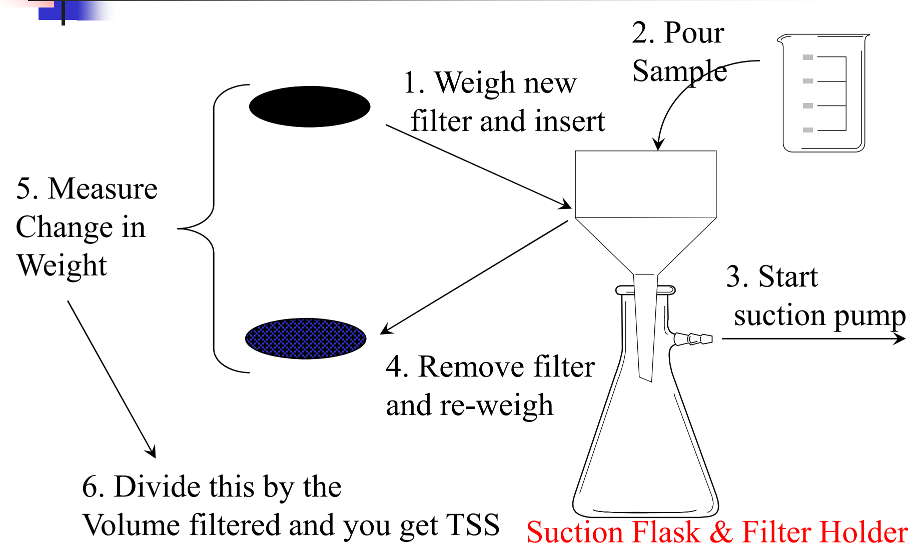


Figure 2-2. The analytical difference between total solids (TS), total suspended solids (TSS), volatile suspended solids (VSS), and total dissolved solids (TDS).

Filtration for Solids Analysis



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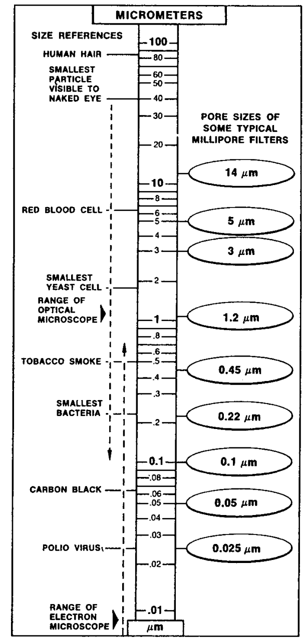
Filtration

- Choice of filter "pore" s
  - Somewhat arbitrary
  - Termed "operational"

From: The Chemist's Companion, by Gordon & Ford



Scale comparing Millipore filter pore sizes with microbes and micro-particles.

Role of heating

General rule: all materials having a significant vapor pressure at the designated temperature are lost.

- Drying @ 103-105ºC (best for low TDS waters)
  - positive bias: waters of crystallization and occluded water
  - some use a steam bath (~98ºC)
- Drying @ 180ºC (best for high TDS waters)
  - positive bias: some waters of crystallization and some partial oxidation of organics
  - negative bias: loss of some volatile organics, and some loss of CO_2
- Charring @ 550ºC (remove organic matter)
  - intended reaction: organics → $CO_2\uparrow + H_2O\uparrow$
  - positive bias for VS: $MgCO_3 \rightarrow MgO + CO_2\uparrow$
  - $NH_4HCO_3 \rightarrow NH_3\uparrow + CO_2\uparrow + H_2O\uparrow$

Procedures

- Total Solids (TS) ±5%
  - evaporated at 103-105ºC for 1 hour
    - vycor or platinum evaporating dishes (procelain absorbs water)
- Total Dissolved Solids (TDS)
  - filtered, then evaporated at 103-105ºC or 180ºC for 1 hour
- Total Suspended Solids (TDS) ±5-10%
    - weigh filter paper & pan; dry together
- Fixed Solids (FS)
  - all matter that remains after heating to 550ºC
- Volatile Solids (VS)
  - all matter that is lost upon heating to 550ºC, but not lost upon drying at 103-105ºC for 1 hour

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Significance (cont.)

- Wastewater
  - measure strength & treatment efficiency (**TS, TSS**)
  - mass balance of solids for operation and sizing of sludge treatment, handling & disposal facilities (**TSS, VSS**)
  - estimate of active biomass for process contol (**VSS**)
  - regulatory control on effluent (**TSS**)
- Natural Waters
  - direct hazard to aquatic life (**TSS, TDS**)
  - indirect hazard due to solubilization of hydrophobics (**TSS**)
  - siltation and hydraulic problems (**TSS**)
  - use for crop irrigation (**TDS**)
- Drinking Waters (uses turbidity in place of TSS)
  - suitability as a water supply (**TDS**), aesthetics, interference with other processes, treatment doses & sizing (Turbidity)

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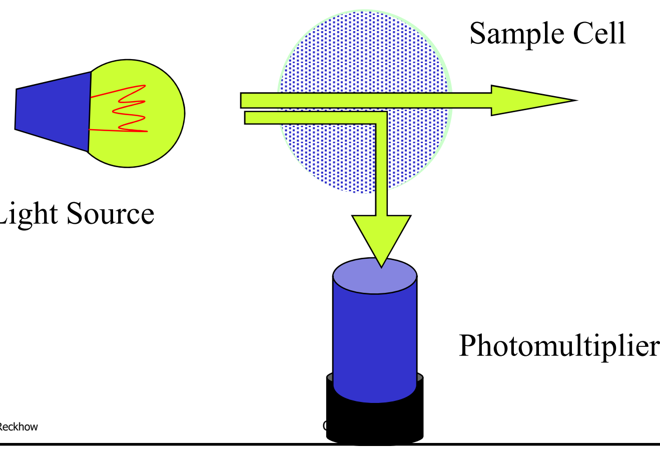
Turbidity

A measure of the clarity of a water. It is determined by light scattering using a turbidimeter.



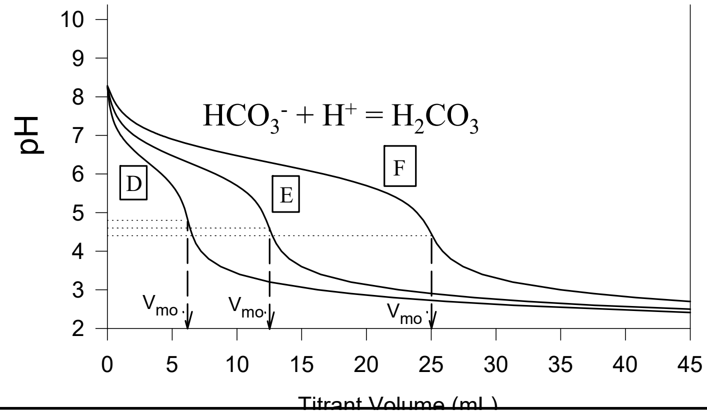
Avg. Concentration Of Major Inorganics in River Water

Species	Global Avg.[1]	N. America Median[2]	Colorado Ave.[3]
Ca^{+2}	13.4	40	83
Mg^{+2}	3.3	10	24
Na^{+}	5.1	31	95
K^{+}	1.3	2.4	5.0
Al^{+3}		0.01	
Cl^{-}	5.7	16.5	82
F^{-}		0.17	
Br^{-}		0.019	
SO_4^{-2}	8.3	33	270
HCO_3^{-}	52	225	135
SiO_2	10.4	16.5	9.3
Total	100	330	703

$$Alk. = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

Alkalinity

- The capacity of a water to neutralize strong acids.
- In Natural waters it is associated with the carbonate and bicarbonate concentrations.



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Other Units

•Calcium Carbonate

Both alkalinity and hardness are usually expressed in either meq/L or mg $CaCO_3$/L

$$Alk. = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

$$Hardness = [Ca^{+2}] + [Mg^{+2}]$$

Because Calcium Carbonate has a gram formula weight (GFW) of 100 g and because there are two equivalents per mole (Z=2), we can say that

$$50\ g\ CaCO_3 = 1\ eq$$

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Nutrients

- Nitrogen: all forms can stimulate growth
  - Ammonia: toxic & oxygen consumer
  - Nitrite: rarely present in high concentrations
  - Nitrate: drinking water concern
  - Organic-N: oxygen consumer
- Phosphorus: stimulate growth
  - ortho-phosphates
  - Organic-P

} Cultural Eutrophication

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Heavy Metals

- Toxic, non-biodegradable, exist in various oxidation states and chemical forms
- Examples
  - Mercury
  - Lead
  - Cadmium
  - Arsenic
  - Others

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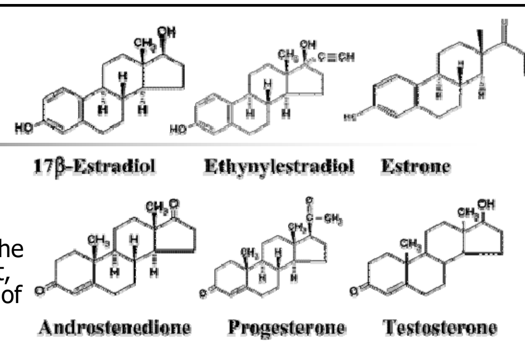
Specific Organic Compounds

- Pesticides
- Volatile Organic Compounds (VOCs)
- Polychlorinated Biphenyls (PCBs)
- Polynuclear Aromatic Hydrocarbons (PAHs)
- Disinfection Byproducts (DBPs)
- Endocrine Disrupting compounds (EDCs) and pharmaceuticals & personal care products (PPCPs)

Endocrine Disruptors



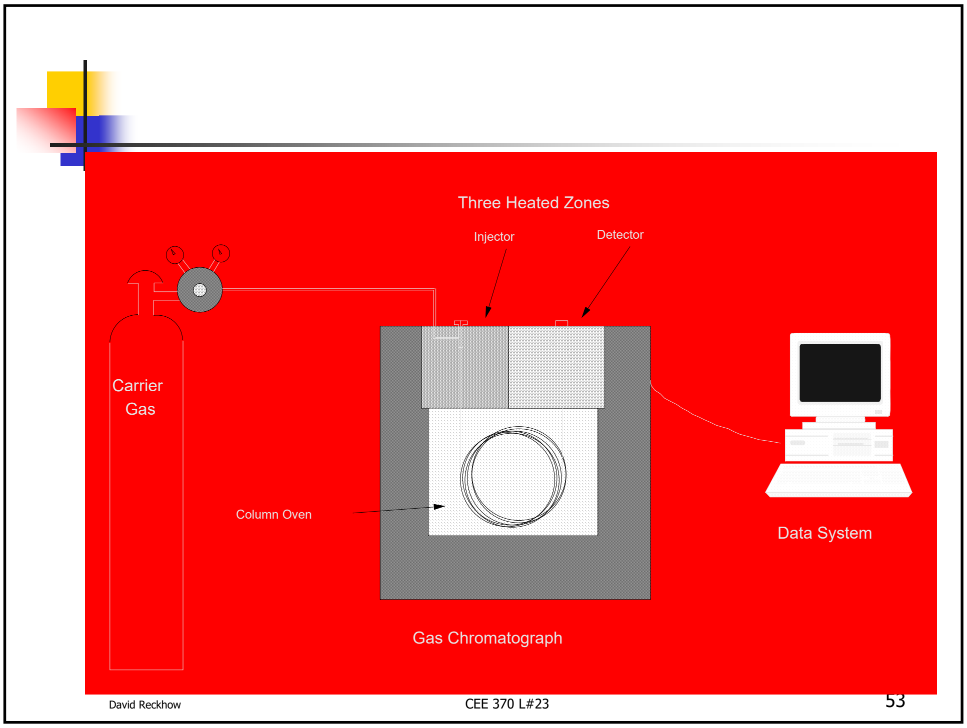
- EDCs:
  - Agents produced outside an organism that interfere with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior
- Androgenic Compounds
  - Compounds that mimic testosterone, the primary male sex hormone
- Estrogenic Compounds
  - Compounds that mimic estrogen, the primary female sex hormone
- Anti-estrogens, or anti-androgens
  - Compounds that block the action of the estrogens & androgens
- Phytoestrogens, phytoandrogens
  - Estrogens and androgens from plant sources

Measuring Specific Organic Compounds

- Cannot use classical methods
- Requires separation
- Chromatography is common
  - Gas
  - Liquid
- Detection: must be sensitive
- Sometimes requires specificity
  - mass spectrometry

Gas Chromatography

- An instrumental method
- Very powerful technique
  - very sensitive
  - can analyzed complex mixtures of organic compounds
- Has revolutionized organic pollutant analysis
- Steps
  - Sample is vaporized
  - Vapor sample is passed though a tube or column that slows down certain compounds
  - Substances are detected and measured as they come exit the tube or column


Three Heated Zones
Injector
Detector
Carrier Gas
Column Oven
Data System
Gas Chromatograph
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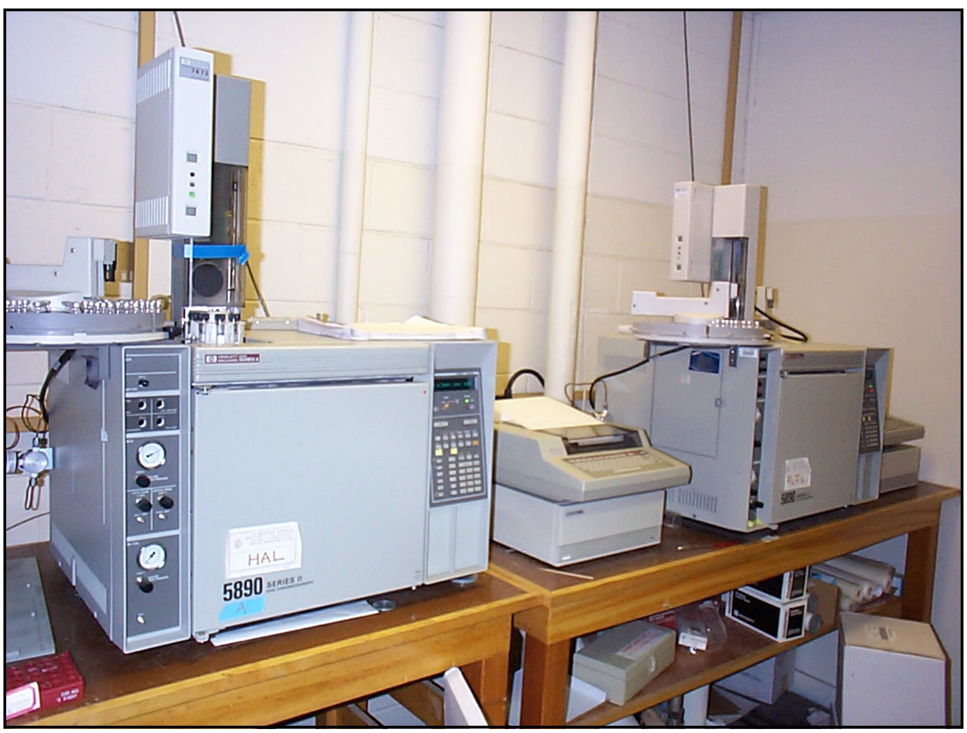
53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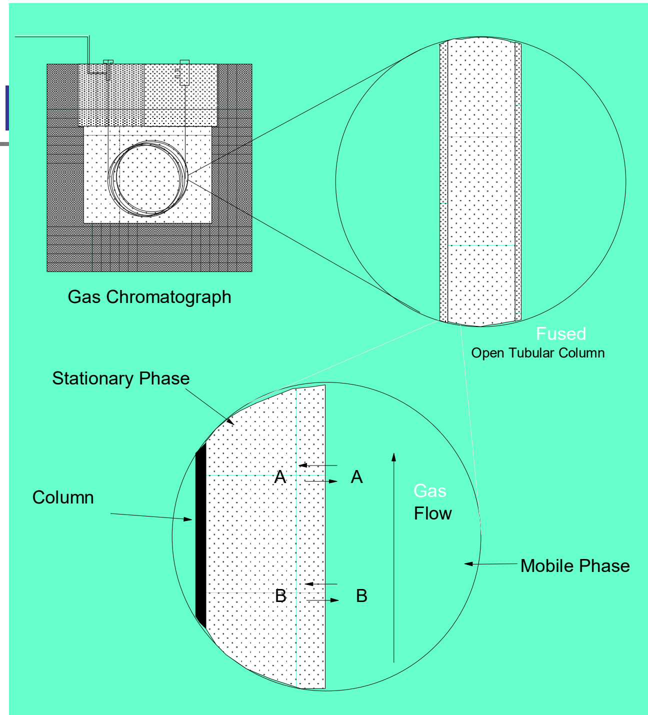

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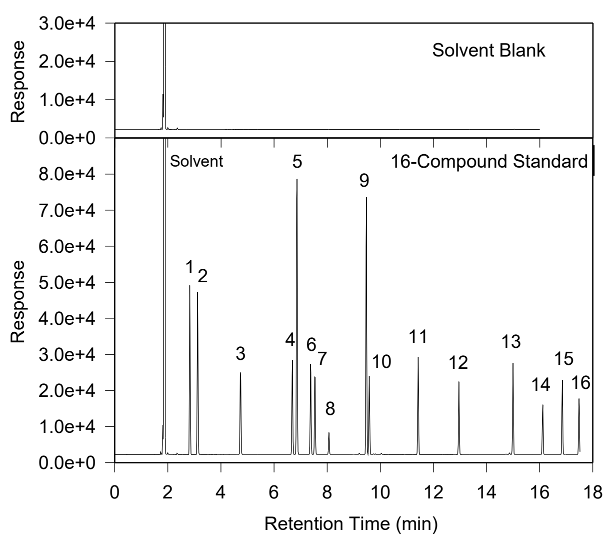
GC Chromatogram of Petroleum Standard



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Compounds in Petroleum Standard

Number	Name	Retention Time (min)
1	2-Methylhexane	2.83
2	2,2,4-Trimethylpentane	3.12
3	3-Methylheptane	4.74
4	Ethylbenzen	6.69
5	m-Xylene	6.86
6	o-Xylene	7.38
7	Nonane	7.54
8	Cumene	8.07
9	1,2,4-Trimethylbenzene	9.48
10	Decane	9.59
11	Undecane	11.42
12	Naphthalene	12.96
13	1-Methylnaphthalene	15.00
14	Tetradecane	16.12
15	2,3-Dimethylnaphthalene	16.85
16	Pentadecane	17.48

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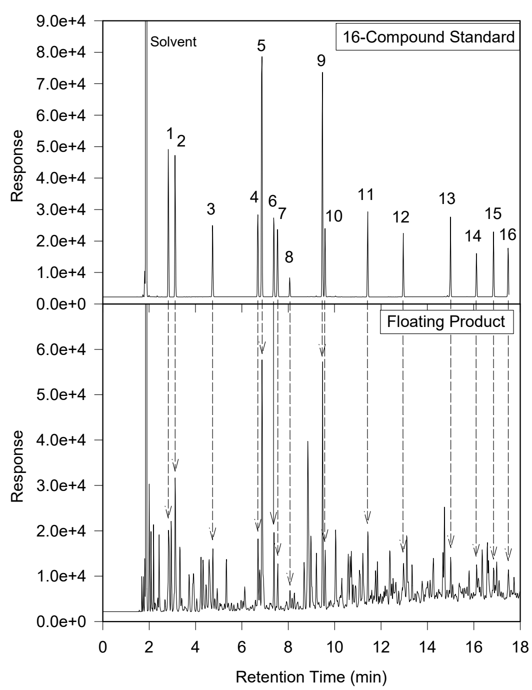
Comparison with Actual Sample



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Water Quality Parameters

Parameter	Health Effects	Typical Conc. Lake or Stream	Drinking Water Standards
Microbiological: Total Coliforms, #/100 mL	Indicator organism, not necessarily disease causing	<100	1
Turbidity, NTU	Interferes with disinfection	1-20	1 to 5
Inorganic: Arsenic, mg/L	Nervous system and dermal effects	<0.01	0.05
Barium, mg/L	Circulatory problems	<0.01	1
Cadmium, mg/L	Kidney effects	<0.01	0.01
Chromium, mg/L	Liver/kidney effects	<0.01	0.05
Lead, mg/L	Nervous system, kidney, highly toxic to infants and pregnant women	<0.01	0.05
Mercury, μg/L	Nervous system, kidney	<0.01	2

WQ Parameters (cont.)

Nitrate, mg/L	Methemoglobinemia	<1.0	10
Selenium, μg/L	Gastrointestinal effects	<1	10
Silver, μg/L	Skin discoloration	<1	0.05
Fluoride, mg/L	Skeletal damage	<1	4
Organics: Endrin, μg/L	Nervous system/kidney	<1	0.2
Lindane, μg/L	Nervous system/kidney	<1	4
Total trihalomethanes, μg/L	Cancer risk	<50	100
Benzene, μg/L	Cancer	<1	5
Other: pH	Corrosivity (not health)	6-8	6.5-8.5

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Typical Municipal WW Charact.

Parameter	Typical Wastewater Characteristics, mg/L except pH	U.S. EPA Discharge Standards, mg/L except pH	Typical Concentrations in Lakes or Streams, mg/L except pH
BOD_5	150-300	30	2-10
Total Suspended Solids	150-300	30	2-20
COD	400-600	N/A	5-50
D.O.	0	4-5	4-Sat.
NH_3-N	15-40	*	<1
NO3	0	*	<1
pH	6-8	6-9	6-8

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- To next lecture

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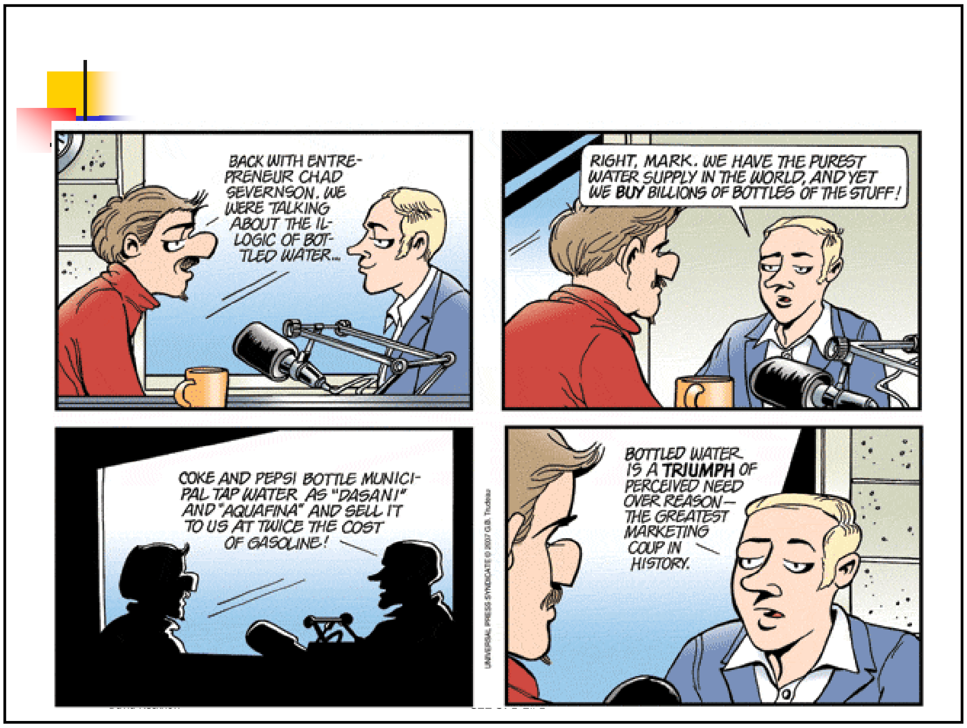
BACK WITH ENTRE-PRENEUR CHAD SEVERNSON. WE WERE TALKING ABOUT THE IL-LOGIC OF BOT-TLED WATER...
RIGHT, MARK. WE HAVE THE PUREST WATER SUPPLY IN THE WORLD, AND YET WE BUY BILLIONS OF BOTTLES OF THE STUFF!
COKE AND PEPSI BOTTLE MUNICI-PAL TAP WATER AS "DASANI" AND "AQUAFINA" AND SELL IT TO US AT TWICE THE COST OF GASOLINE!
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