#### Lecture 4: Parameter Measurements

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Objective: To introduce parameters to indicate pollution and methods to measure them

#### Previous class: Parameters

- Suspended solids
- Pathogens
- Inorganic ions
- Organic compounds
- Excess nutrients
- Oxygen demanding wasters
  - Estimated stoichiometrically by theoretical oxygen demand (ThOD)
  - biochemical oxygen demand (BOD)
  - Nitrogenous oxygen demand (NBOD)
  - chemical oxygen demand (COD)

# Solids

- Used in controlling biological process; drinking water quality, etc.
- Gravimetric analysis is based on the determination of constituents or categories of materials by measurement of their weight.
- Three analytic operations: filtration, evaporation, and combustion.
  - Filtration is used to separate suspended or particulate (non-filterable) fraction from dissolved or soluble (filterable) fractions.
  - Evaporation separates water from material dissolved or suspended in it.
  - Combustion differentiates between organic and inorganic matter.
    Organic matter will be destroyed completely by burning at 550°C for 30 min.

Ref: AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (2540 D. Total Suspended Solids Dried at 103-105°C; 2540 E. Fixed and Volatile Solids Ignited at 550°C)

# Total Suspended Solids

#### **Procedure:**

 Filter samples (50 ml); Oven dry at 103°C for 30 min; At this stage all water will be evaporated and only suspended solids will be retained on filter.

#### Total suspended solids

mg total suspended solids = 1000\*(A-B)/(sample volume in mL) (1)

Weight crucibles (mass=C) and then weight crucible and filter (total mass=E); Initial filter weight=B; Weigh filters now (mass =A g).

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# Volatile and Fixed Suspended Solids

- Put crucibles with filter paper in muffle furnace and Ignite at 550°C for 15 min. At this stage all volatile components of solids will be volatilized and only fixed inert solid materials will be left in crucible. Weigh crucible after proper cooling (mass=D g).
- Volatile suspended solids (F) :

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mg volatile suspended solids/L = 1000*(E-D)/(sample volume in mL) (2)
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Fixed suspended solids (G):

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mg volatile suspended solids/L =1000*(D-C)/(sample volume in mL)
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#### **Parameters**

- Oxygen demanding wastes
- Pathogens (parameters: indicators: fecal coliforms, total coliforms, coliphage; direct measurement of pathogens)
- Inorganic ions (arsenic ions; chromium ions, nitrates; phosphates)
- Excess nutrients (ammonium ions; phosphates)

#### BOD

The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called biochemical oxygen demand (BOD)

Organic matter + 
$$O_2$$
  $\longrightarrow$   $CO_2$ +  $H_2O$  + New Cells + Stable Products

#### BOD

- It is expressed in mg of oxygen required per liter of wastewater (mg/L)
- The five-day BOD (BOD<sub>5</sub>) is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation

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# Unseeded BOD test

- Put a sample of wastewater into a 300 mL bottle
- Incubate for 5 days at 20°C, in the dark, and with stopper on.
- Measure concentration of dissolved oxygen (DO) in the beginning, and 5 days later
- Need at least 2 mg DO change in 5 days
- Usually need to dilute with water (oxygen saturated)

$$BOD_5 = \frac{DO_i - DO_f}{P}$$

P = dilution factor = volume of wastewater/total volume

DO<sub>i</sub> = initial dissolved oxygen

DO<sub>f</sub> = final dissolved oxygen



## Seeded BOD Test

- Take sample of waste, dilute with oxygen saturated water, add nutrients and microorganisms (seed)
- Measure dissolved oxygen (DO) levels over 5 days
- Temperature 20°C, In dark (prevents algae from growing)
- Final DO concentration must be > 2 mg/L
- Need at least 2 mg/L change in DO over 5 days

$$BOD_5 = \frac{(DO_i - DO_f) - (B_i - B_f)(1 - P)}{P}$$

P = dilution factor = volume of wastewater/total volume  $DO_i$  and  $DO_f$  = initial and final (5 d) DO conc. of diluted sample  $B_i$  and  $B_f$  = initial and final (5 d) DO conc. of seeded diluted water (blank)

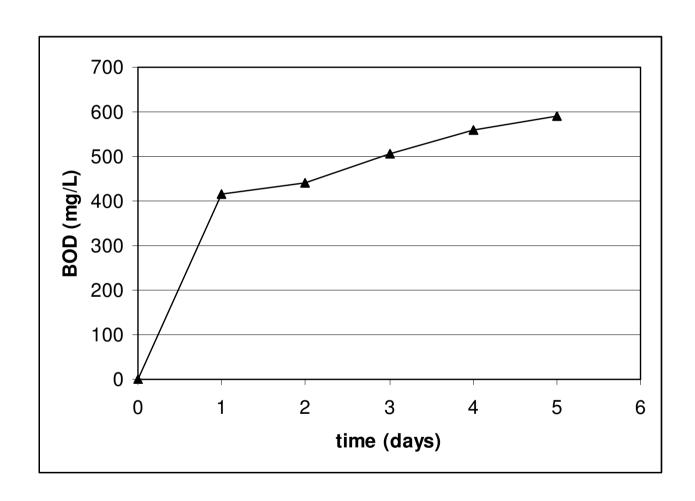
# Example 1

 A BOD test was conducted in the laboratory using wastewater being dumped into Lake Spartan. The samples are prepared by adding 3 mL of wastewater to the 300 mL BOD bottles. The bottles are filled to capacity with seeded dilution water.

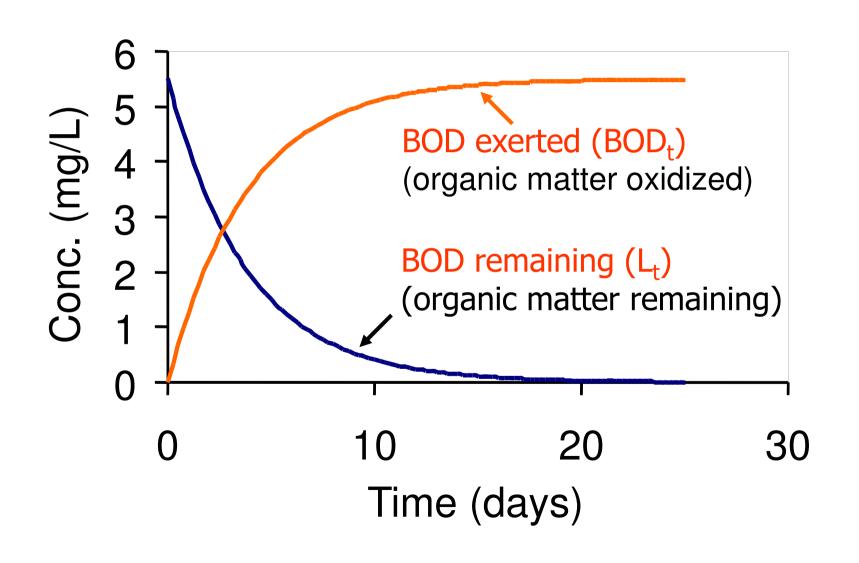
#### Example 1

Time	Diluted	Blank Seeded
(days)	sample	Sample DO
	DO (mg/L)	(mg/L)
0	7.95	8.15
1	3.75	8.10
2	3.45	8.05
3	2.75	8.00
4	2.15	7.95
5	1.80	7.90

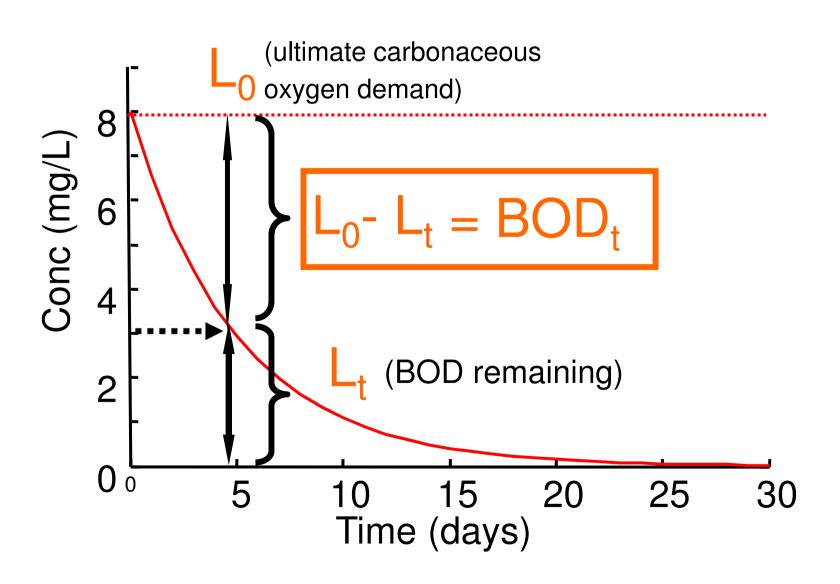
#### Example 1



### Modeling BOD, L<sub>t</sub> and L<sub>0</sub>



# Modeling BOD, L<sub>t</sub> and L<sub>0</sub>



### Modeling BOD, L<sub>t</sub> and L<sub>0</sub>

At any time,  $L_0 = BOD_t + L_t$  (ultimate BOD equals the amount of DO demand used up and the amount of DO that could be used up eventually)

$$\mathsf{BOD}_t = \, \mathsf{L}_0 - \, \mathsf{L}_t$$

- Replace  $L_t$  using:  $L_t = L_o e^{-kt}$
- To give:  $BOD_t = L_o L_o e^{-kt}$
- Simplified to:  $\longrightarrow$  BOD<sub>t</sub> = L<sub>o</sub>(1-e<sup>-kt</sup>)

# Chemical Oxygen Demand

- Chemical oxygen demand similar to BOD but is determined by using a strong oxidizing agent to break down chemical (rather than bacteria)
- Still determines the equivalent amount of oxygen that would be consumed
- Value usually about 1.25 times BOD

#### COD measurement

- Potassium dichromate is a strong oxidizing agent and it can be used to prepare solution of exact normality.
- $C_nH_aO_bN_c+d Cr_2O_7^{2-} + (8d+c) H^+ => nCO_2 +[(a+8d-3c)/2]H_2O+c NH_4^+ +2dCr^{3+} (1)$
- Here d=(2n/3)+(a/6)-(b/3)-(c/2)

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# Nitrogenous Oxygen Demand

- So far we have dealt only with carbonaceous demand (demand to oxidize carbon compounds)
- Many other compounds, such as proteins, consume oxygen
- Additional oxygen demand required when nitrogen compounds are oxidized

Nitrification (microorganisms convert ammonia to nitrite)

$$2 \text{ NH}_3 + 3\text{O}_2 \rightarrow 2 \text{ NO}_2^- + 2\text{H}^+ + 2\text{H}_2\text{O}$$
  
 $2 \text{ NO}_2^- + \text{O}_2 \rightarrow 2 \text{ NO}_3^-$ 

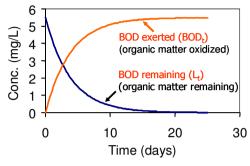
Overall reaction:

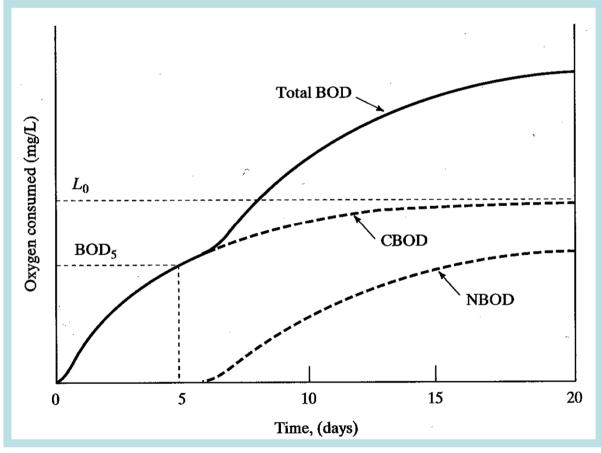
$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

- NBOD = oxygen needed to convert NH<sub>3</sub> to NO<sub>3</sub><sup>-</sup>
- Theoretical NBOD can be determined using the ratio:

$$\frac{\text{g oxygen used}}{\text{g of nitrogen used}} = \frac{(2 \text{ moles}) \left(\frac{32 \text{ g}}{\text{mole}}\right)}{(1 \text{ mole}) \left(\frac{14 \text{ g}}{\text{mole}}\right)} = \frac{4.57 \text{ g O}_2}{\text{g N}}$$





#### **Questions to think**

- Why do the COD analysis and BOD analysis give different results for the same waste?
- What could be inferred from the following samples concerning the relative ease of biodegradability: Sample A (5-d BOD/COD=24/30) and Sample B (5-d BOD/COD=10/50)?

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HW1 (no submission)

